DIPLOMA THESIS

Impact of Temperature, Light and Storage time on Bituminous Materials measured with FTIR Spectroscopy

Submitted in satisfaction of the requirements for the degree of
Diplom-Ingenieur
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DIPLOMARBEIT

Einfluss von Temperatur, Licht und Lagerungsdauer auf bituminöse Materialien, gemessen mit FTIR-Spektroskopie

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Kurzfassung

Bitumen ist ein schwarzes Material, das bei der Raffination von Rohöl gewonnen wird. Es wird hauptsächlich als Bindemittel in Asphaltstraßen, sowie aufgrund seiner wasserabweisenden Eigenschaften im Bereich der Dachabdichtung und diverse anderen hydraulischen Anwendungen eingesetzt. Als organisches Material altert Bitumen mit der Zeit. Im Allgemeinen gibt es zwei Alterungszustände von Bitumen (Kurz- und Langzeitalterung), die im Labor mit standardisierten Methoden stimuliert werden können. Der Rolling Thin Film Oven Test (RTFOT) repräsentiert den Kurzzeit-Alterungszustand des Bindemittels, während der Pressure Aging Vessel (PAV) den Langzeit-Alterungszustand des Bindemittels darstellt.

Bitumencharakterisierung basiert primär auf einfachen mechanischen Untersuchungsmethoden. Auf Grund der chemischen Komplexität des Materials, ist dies aber nicht ausreichen, um das Material zu charakterisieren. Deshalb haben in den letzten Jahrzehnten die chemischen Untersuchungen drastisch zugenommen. Die Fourier-Transformations-Infrarot-Spektroskopie (FTIR) ist eine der beliebtesten spektroskopischen Methoden für chemische Untersuchungen von Bitumen. Der Grund dafür ist die Einführung der abgeschwächten Totalreflexion (ATR), die die Arbeit erleichtert hat. Die ATR-FTIR-Spektroskopie ist eine empfindliche Oberflächenmethode und erfordert sehr genaues Arbeiten, wenn es um empfindliche Materialien wie Bitumen geht.

Es gibt zwei Hauptaufgaben dieser Diplomarbeit, die sich mit den Auswirkungen der Probenvorbereitung für die ATR-FTIR Spektroskopie befassen:

- Temperatur und Heizzeit (Dauer)
- Bedingungen und Lagerzeit

Für diese Studie wurden sechs Arten von Bindemitteln untersucht, vier davon aus derselben Rohölquelle, aber mit unterschiedlichen Spezifikationsklassen (drei unmodifizierte und ein polymermodifiziertes) und zwei weitere aus verschiedenen Rohölquellen mit denselben Spezifikationsklassen (beide unmodifiziert). Die Untersuchung wurde mit 5 g Bindemittel durchgeführt, das 5-30 Minuten lang bei 180°C erhitzt wurde. Im Laufe dieser Arbeit wird sich zeigen, dass die Oxidation des Bindemittels beim Erhitzen auf 180°C für bis zu 30 Minuten keinen großen Einfluss hat, wenn man gut mit ihm umgeht (das Verfahren wird später vorgestellt). Andererseits kommt es bei der Lagerung der Proben, insbesondere im Tageslicht,

zu einer erheblichen Oxidation der Bindemitteloberfläche. Daher wird empfohlen, das Bindemittel 5 - 10 Minuten lang zu erwärmen und in einem klimatisierten Raum zu lagern. Außerdem sollten die Proben abgedeckt werden, damit sie nicht direkt mit dem Tageslicht in Berührung kommen, und die Messung sollte innerhalb einer Stunde nach ihrer Herstellung erfolgen.

Abstract

Bitumen is a black material, which is derived from the crude oil refinement process. It is widely used as a binder in asphalt pavement and due to its waterproofing properties, bitumen is also used for roofing and for several hydraulic application. As an organic material, bitumen ages with time. In general, there are two aging states of bitumen (short and long–term aging), which can be stimulated in the laboratory with standardized methods. Rolling Thin Film Oven Test (RTFOT) represents the short–term aging state of the binder, where Pressure Aging Vessel (PAV) represents the long–term aging state binder.

Bitumen characterization is mainly performed using a variety of conventional mechanical tests. However, these tests fail to uncover the complex chemical composition of the material. Thus, in the past decades chemical investigation has increased drastically. Fourier transform infrared spectroscopy (FTIR) is one of the most popular spectroscopic methods for chemical research. The reason for this is that the attenuated total reflection (ATR) has been implemented, which has facilitated the work.

ATR-FTIR spectroscopy is a sensitive surface method and requires very precise work when dealing with sensitive material such as bitumen.

There are two main tasks of this Diploma Thesis on the impact of sample preparation:

• Temperature and heating time

• Conditions and storage time

There were six types of binders investigated for this study, four of them from the same crude oil source but different specification classes (three unmodified and one polymer modified) and two others from different crude oil sources with the same specification classes (both unmodified). The investigation was done with 5g of binder heated at 180°C for 5-30 min. Throughout this thesis, it will be seen that there is not an enormous impact on the oxidation of binder when heating at 180°C for up to 30 min when handling well with it (the procedure will be presented later). On the other hand, when storing the samples, especially in the light, significant oxidation on the binder's surface occurs. Therefore, it is recommended to heat the binder for 5 – 10 min and stored it in a climatized room. In addition, the samples should be covered so that they do not come into direct contact with daylight, and the measurement should be taken within one hour of their preparation.

Acknowledgments

First and foremost, I would like to thank God for guiding me on the right path and giving me health, courage and strength to achieve my goals in life.

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I would like to thank my friends for always being there for me in good times and in hard times and for always pushing me forward.

Finally yet importantly, I would like to thank my parents, my brother and my two beloved sisters for their sacrifice, unconditional love, care and support during this wonderful journey.

Contents

1 Introduction

Bitumen is a black, viscous, organic and stable at ambient temperature material obtained from petroleum refining and used as a binder in asphalt mixtures with aggregates and in roofing membranes due to its waterproofing properties. This makes bitumen very important for people's lives, because life without bitumen, therefore without asphalt roads, would have been unimaginable. Bitumen has a direct impact on our society, economy and industry. Thus, it has improved and facilitated the life of the community. As the only organic material in the asphalt mixture, bitumen is severely affected by environmental factors such as mechanical stress, UV and visible light, reactive gasses from the atmosphere, wide temperature ranges, etc. As a result, it is subject to aging during its service life. As bitumen ages, its viscoelastic properties change, becoming more brittle and stiffer. Thus, its chemical composition changes too.

There are two aging states of the bitumen, short- and long-term aging. The short-term aging can be simulated in the laboratory with Rollin Thin Film Oven Test (RTFOT), which corresponds to the process that bitumen undergoes during transport, mixing and paving. Short-term aging is induced by high temperatures and oxygen uptake, that happens within few hours. Long-term aging of the binder results in slow oxidation due to environmental factors such as temperature fluctuations, oxygen, ozone, etc. Long-term ageing can be simulated in the laboratory with Pressure Aging Vessel. (PAV). This aging state corresponds to the period of five to ten years of the bitumen during its service life after application.

The aim of this Diploma Thesis is to answer the question on how to handle such a sensitive material as bitumen, before it shows significant signs of ageing.

The structure of this thesis is as follows: Theoretical paradigm, general information and the methods that has been used are presented in Chapter 2. Materials and methods in Chapter 3. A detailed presentation of the results and a discussion are presented in Chapter 4 and Chapter 5. At the end summary and conclusion is presented in Chapter 6.

2 Theoretical Paradigm

2.1 Bitumen

Bitumen is a black, sticky and almost non – volatile mixture of different organic molecules. It is resistant to chemicals and polar solvent but soluble in organic solvents (toluene, gasoline etc.). Bitumen is manufactured from distillation of crude oil as the last product obtained from refining process after suitable petroleum oils are recovered. Bitumen has replaced tar, which was previously used in road construction, roofing membranes etc. Tar is cancerous in the human body, therefore use of tar has been forbidden[1, 2]. Most of the bitumen is used in Asia and Pacific (37%) (see Figure 1 left), followed by North Amerika (25%), European Union (17%), Europe Other (11%), South America (7%) and the lowest country that uses bitumen is Africa with only 3%. Bitumen is used approximately 85% as a binder for pavement of roads, airports, parking lots etc., 10% in roofing and 5% for secondary uses, as shown on the left side of Figure 1 [3].
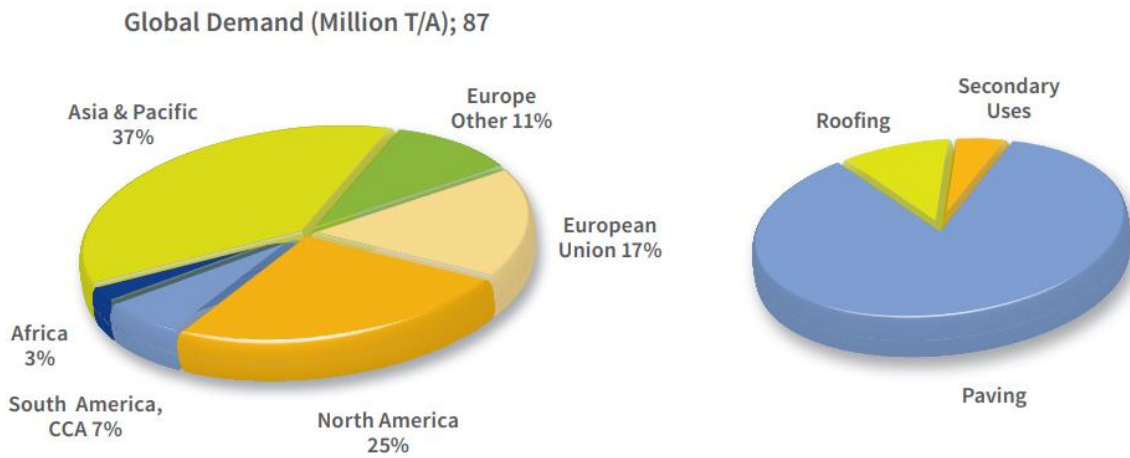

Figure 1: Bitumen use in countries (left) and application (right)[3]

2.2 Bitumen Manufacture

Bitumen is a product of crude oil obtained from petroleum refinery. First, crude oil is heated (350-400°C) in a tubular furnace than under atmospheric pressure in distillation column its lighter compounds such as methane, ethane, propane gases etc., using different boiling temperatures, are removed. Distillation products drop off into the trays of distillation column. After first step, the remaining gasoil undergoes a vacuum distillation at a reduced temperature

and at a reduced pressure of approximately 50 mbar, where it is separated into heavier products (lubricating oils, kerosene). The heaviest product that remains is bitumen, which can be converted into oxidation bitumen (blowing of air), polymer bitumen (addition of polymer) or bitumen emulsion (adding of water and emulsifier)[1].
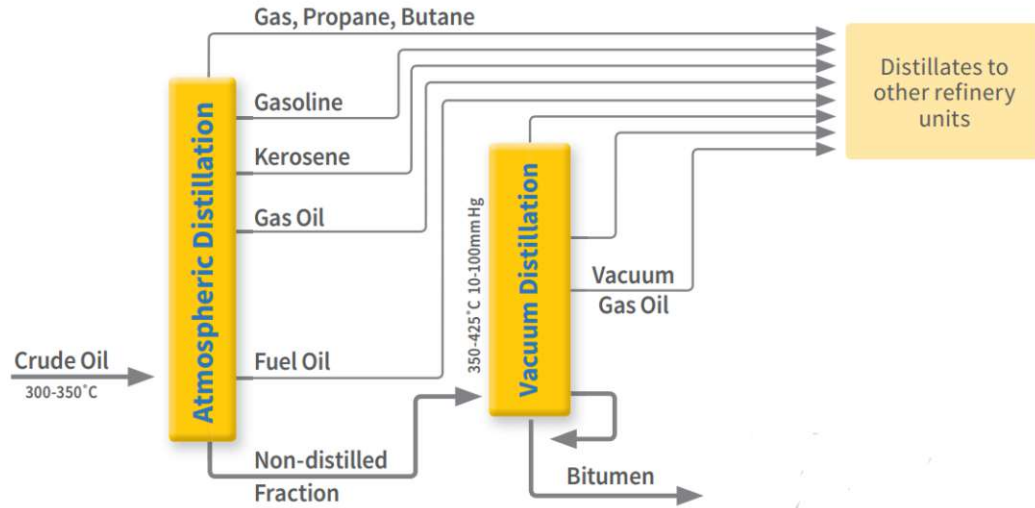

Figure 2: Bitumen recovery from crude oil [3]

2.3   Classification -Needle Penetration Test

Penetration test is performed to determine the consistency of the bitumen, following the EN 1426:2015[4]. Such a test is performed by applying a needle with 100 g load into a bituminous sample. The amount that needle penetrates is measured in tenth of millimeter unit after 5 seconds at 25°C, as shown in Figure 3.
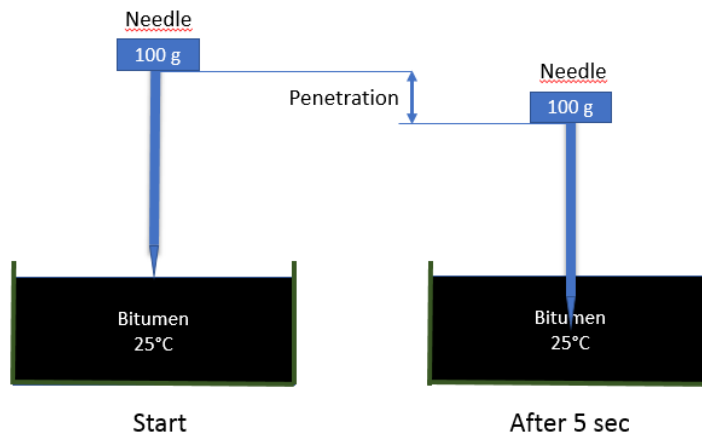

Figure 3: Needle penetration test drawing

2.4   Bitumen Aging

Bitumen has three aging states: unaged, short-and long-term aged. With aging, hardness of the material will increase. Unaged bitumen is also known as fresh bitumen from refinery which is ready to use. Aging that occurs during mixing, hot storage, transport, and application is a so-called short-term aging. Aging after five to ten years of service life is a so-called long-term aging [5].

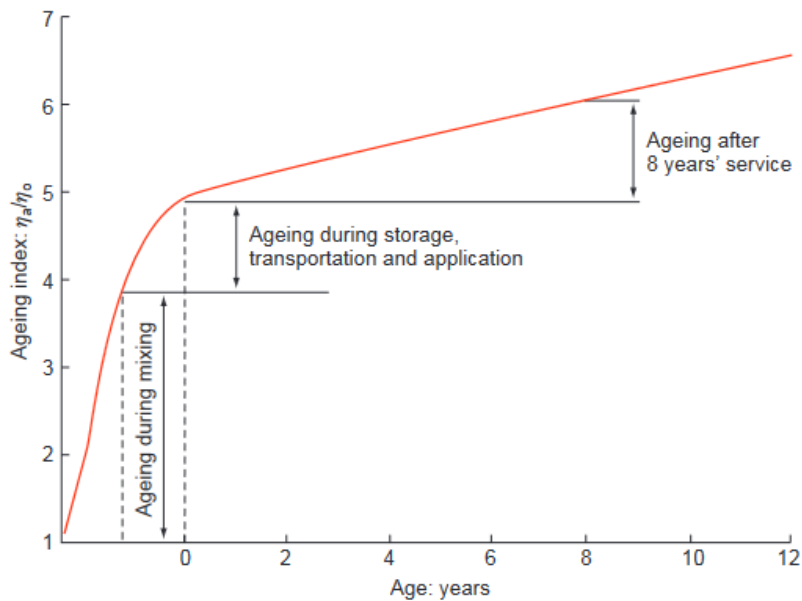 Aging states and change of viscosity are shown in Figure 4.

Figure 4: Schematic representation of bitumen aging [6]

The laboratory short- and long-term aging of bitumen is presented below.

2.5   Laboratory Bitumen Aging

2.5.1   RTFOT

The **R**ollin **T**hin **F**ilm **O**ve **T**est (RTFOT) is a method for short term aging of bitumen simulated at laboratory conditions. This method corresponds to the time period between heating bitumen (>130°C) and mixing it with aggregates until asphalt paving. At the same time, it is the fastest oxidation that occurs during its lifetime. The bitumen is poured into glass containers, which are blown with air into a heating chamber at 163°C for 75 min, resulting in rapid oxidation of the bitumen. EN 12607-1 [7]
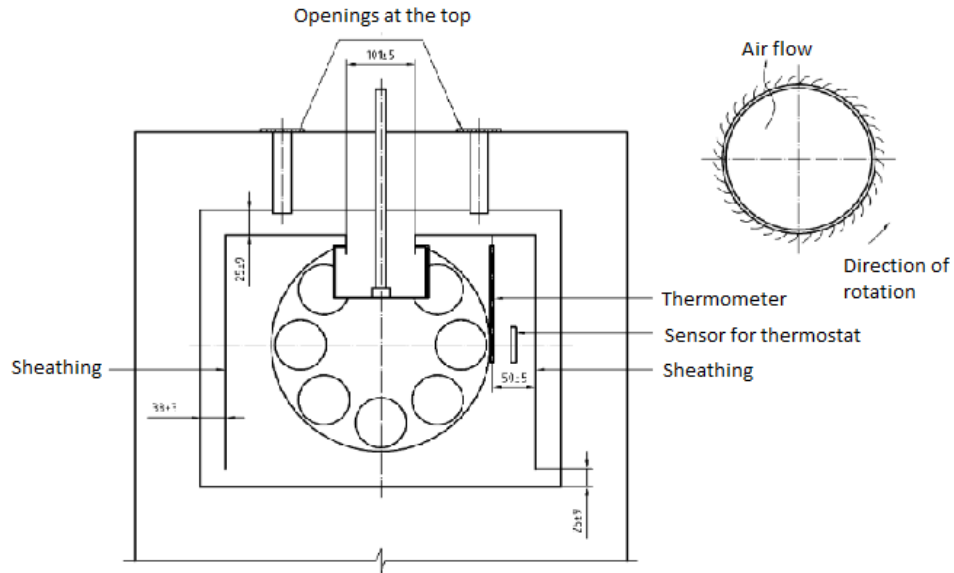
Figure 5: Schematic representation of RTFOT heat chamber (left) and squirrel cage fan (right) [7]

2.5.2 PAV

Long term aging of the bitumen is performed using **P**ressure **A**ging **V**essel (PAV). The RTFOT – aged bitumen (~50g) is placed in metal containers and processed under high pressure (2,1 MPa) at a pressure vessel for the specified period of time (20h) and heat (90 – 110°C). This method corresponds the service life of the bitumen, although it cannot fully encompass the external influences to which the bitumen is exposed during field aging. EN 14679 [8].
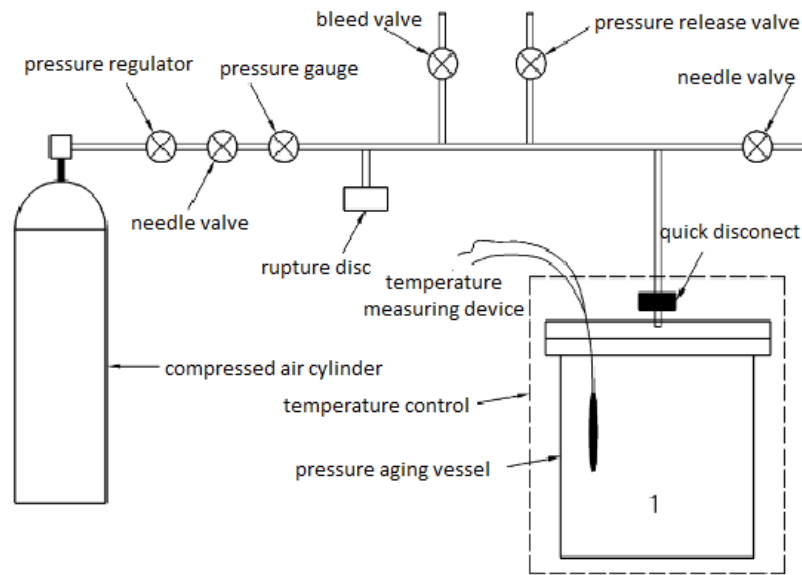

Figure 6: Schematic representation of an PAV test system. EN 14679 [8]

2.6 ATR – FT-IR Spectroscopy

As mentioned above, as the binder ages, its chemical composition changes. Therefore, chemical investigation is of great importance. The most suitable method for this is Fourier Transform Infrared Spectroscopy (FTIR) as the method is very efficient to analyze the substances in every state matter.

Infrared (IR) spectroscopy is mainly focused on the interaction between infrared radiation and the molecules. A part of radiation that has hit the molecule is absorbed by the molecules itself and the rest of the radiation that has not been absorbed is then detected. Furthermore, the radiation causes the vibration of the molecules and stimulates the rotation of them. Information about molecules can be observed based on the intensity and wavelength of the unabsorbed radiation which varies between $500 - 0.75$ µm. Normally, the Infrared is described by the wave number which is inversely proportional to wavelength [9]. There are several types of spectral range of the infrared radiation: mid-, near- and far Infrared. The sources of for infrared radiation usually are incandescent lamps or more specifically tungsten band lamps, quartz halogen light bulbs and LED [10].

The vibrations of the molecules depend on the motion of the atoms which move in translational motion and rotational motion. The molecule with N atoms has 3N motions. These are 3 translational motions and 2 (for linear molecule) or 3 (for nonlinear molecule) rotational motions. Therefore, the equation for linear molecule is $3N - 5$ and for nonlinear molecule is $3N - 6$ which in reality is the number of the vibrational modes. In order to understand the motion of the atoms during the vibration, they need to be in normal coordinates Q_i, however dipole moment μ has to change with the direction of the vibration as in that case the molecule is in excited state as expressed below [10]:

$$\left(\frac{\partial \mu}{\partial Qi}\right) \neq 0 \qquad (1)$$

The vibrational modes are either in harmonic or anharmonic displacement of the atoms from their equilibrium positions. In the Figure 7 the harmonic potential line (dashed line) is valid only for low values of the vibration number, which is also described in the equation 2,

$$V_{iv} = hv_i \left(v_i \frac{1}{2} \right) \qquad\qquad (2)$$

V$_{iv}$ – Vibrational energy state,

H – Planck's constant,

v$_i$ – fundamental frequency of particular mode and

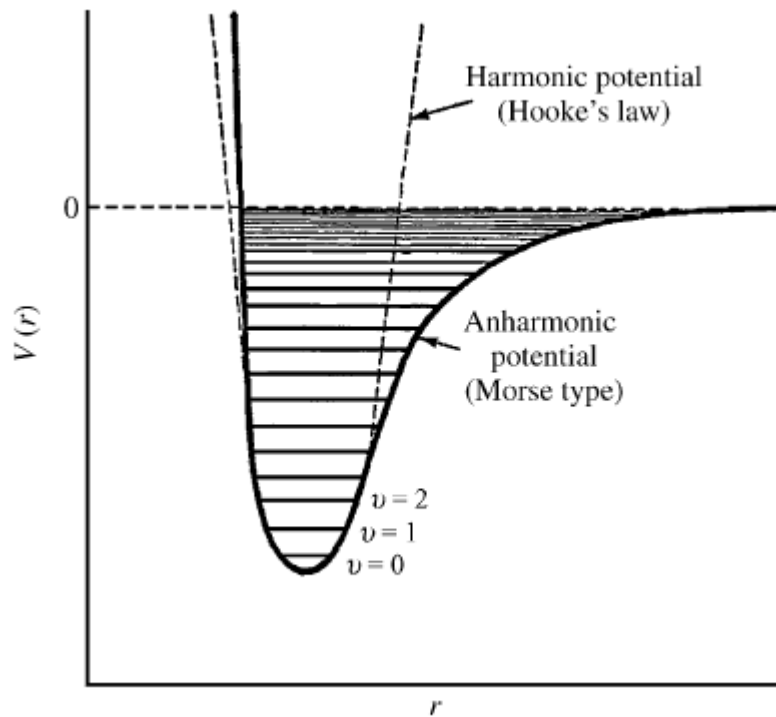v_i – vibrational quantum number of the mode

Figure 7: Schematic view of harmonic and anharmonic potential line [10]

therefore, anharmonic potential function must be used to calculate vibrational energy state (V$_{iv}$)(see equation 3)[10]:

$$V_{iv} = hv_i \left(v_i \frac{1}{2} \right) + hv_i x_i \left(v_i \frac{1}{2} \right)^2 \qquad\qquad (3)$$

X$_i$ – anharmonic constant

Attenuated total reflection (ATR) is one of the most known reflection techniques in the infrared spectrometry. The reasons why this technique is mostly used is because it doesn't enquire samples preparation, therefore is very efficient and no specific expertise is required. This technique is better than the other techniques also because when having materials that are absorptive, it allows the measurement of the infrared spectra much better [11].

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When the sample is coming into the contact with crystal, the light is sent to the crystal on certain angle know as critical angle (θ_c). In order for the light to reflect, the angle of incidence must be larger than the critical angle as it can be seen in Figure 8 [11].
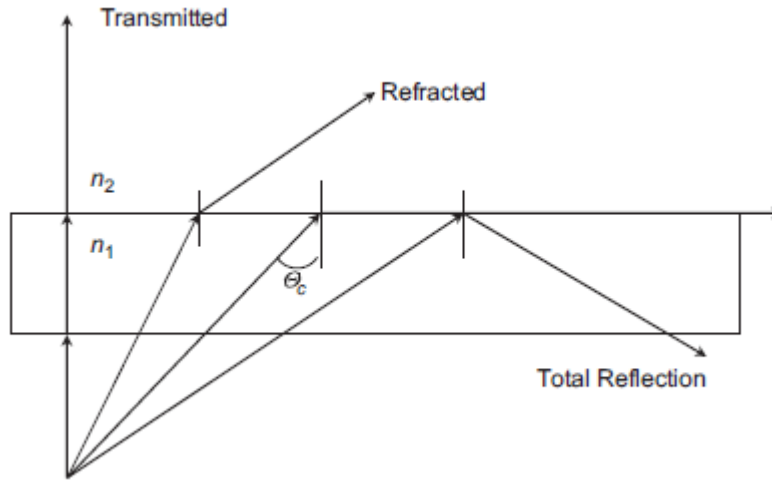

Figure 8: Schematic view of the angle of incidence and critical angle [11]

Real parts of the refractive indices of sample and crystal are important because they are a function for the indices angle as shown in equation below [11]:

$$\theta_c = \sin^{-1}\left(\frac{\eta_2}{\eta_1}\right) \tag{4}$$

η_1 – refractive index of the crystal

η_2 – refractive index of the sample

η is refractive index which consists of real and imaginary component. Whereas on the real part happens when there is no absorption, and the imaginary part happens when there is an absorption. The total absorption (A) can be calculated with the following equation as a function of [11]:

$$A(\theta) = \int_0^\infty \alpha(z)e^{-z/dp}\,dz \tag{5}$$

z – depth into the sample

$\alpha(z)$ – absorption coefficient

The evanescent wave penetrates into the material and this penetration depth is calculated with the following expression[11]:

$$d_p = \frac{\lambda}{2\pi n_p \left(\sin^2\theta - n_{sp}^2\right)^{1/2}} \tag{6}$$

θ – angle of incidence

n_{sp} - ratio of refractive index

The distance from the IRE-sample boundary at which the intensity of the evanescent wave decays is known as the depth of penetration. The depth of the sampling is wavelength dependent. With decreasing of wavenumber, sampling depth decreases.

3 Materials and Methods

3.1 Materials

During this Diploma Thesis, six different binders were used. Four binders are from the same crude oil source but with different specifications classes (Binder A – D). Furthermore, two additional binders from different crude oil sources with the same specification class were also investigated (Binder E and F).

Table 1: Used bitumen for this study

Binder	Crude oil source	Needle penetration	PG grade
A	X	50/70	PG 64-28
B	X	70/100	PG 58-28
C	X	160/220	PG 46-34
D	X	45/80-65	PG 82-28
E	Y	70/100	PG 58-28
F	Z	70/100	PG 64-28

The main objective of this study was to investigate how much thermal stress can be applied and how long bitumen can be stored before it shows significant oxidation detectable by the FTIR spectrometer. Since any changes occurring due to any external factors are most notable at an unaged state because the binder at this stage is not exposed to external factors therefore it didn't oxidize much, all initial experiments were conducted at said virgin ageing state. Furthermore, all binders were also investigated in short-term aged state, except binder B, which was investigated also in long-term aged state.

3.2 Sample Preparation

For sample preparation 5 g for each binder was placed in a metal can (d: 40 mm, h: 13 mm) and then heated at a temperature of 180°C. This temperature was chosen, so all the binders can reach the workable state, especially binder D, which is a PmB (**P**olymer **m**odified **b**itumen) and needs more time and temperature to reach the workable state. The heating time span ranged from 5 to 30 min.

Two different devices were used to heat up the binder, which are displayed in Figure 9:

- heating plate (ARGO LAB M2-A) and
- ventilated oven (Binder FD 23)

Figure 9: Devices used to heat the bitumen: Heating plate (left) and oven (right)

While placing the metal can on the heating plate, the binder was stirred continuously with a thermometer to avoid any inhomogeneity while preparing the samples. Another advantage of stirring with a thermometer is that the temperature can be monitored so that it is able to detect unexpected temperature exceedances. However, continuous stirring can also be a disadvantage, as it can lead to higher incorporation of oxygen thus higher levels of oxidation. On the other hand, when placing the metal can in the oven, the sample cannot be stirred. As the oven is ventilated, the air, which is at much higher temperature than the air in the laboratory, can blow direct on the bitumen surface and cause a significant oxidation. Another problem is the inhomogeneity of the sample due to not being able to stir it. After identifying the problem with the hot air blowing over the bitumen film, several other tests were performed with placing a closed metal can in the ventilated oven. Later on, it will be seen that covering the can with a metal lid, will have a huge impact on reducing the rapid oxidation of the binder.
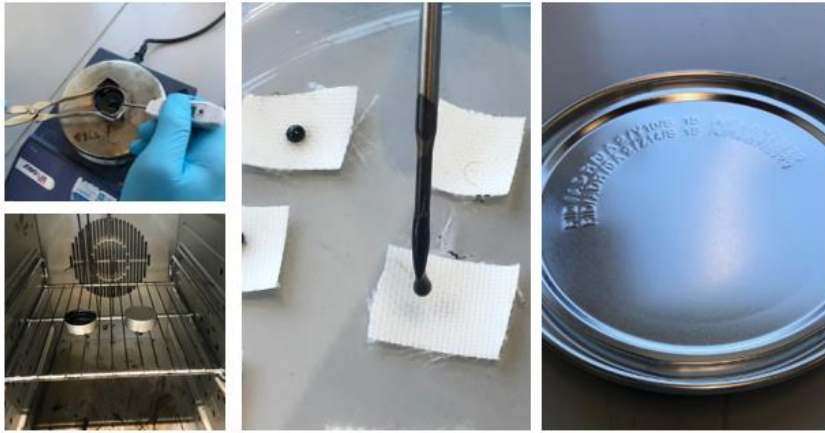
Figure 10: Sample preparation on the heating plate and in the ventilated oven

All binders reached the temperature of 180°C in less than 5 min, so it could be proceeded with sample preparation. Four samples were prepared for each type of binder after 5, 10, 20 and 30 min of heating on the heating plate (see Figure 10 top left) and in the ventilated oven (see Figure 10 bottom left). Before taking the droplets, the liquid binder was stirred one last time to homogenize the binder. Droplets were applied onto a sufficient substrate, in this case, it is a silicon foil (see Figure 10 middle). Silicon foil can be used many times, since the bitumen doesn't stick on it. Alternatively, a piece of paper could be used as well.

After samples were collected in a time frame of 5 to 30 minutes, each at their respective time, the procedure for measuring the samples began with their transfer to the ATR crystal. For the samples collected after 5 minutes, the measuring took place about 25 minutes after their collection, which was sufficient for them to cool down in the room temperature. A crystallization dish was used to place all the substrates with droplets. It should be noted that they were covered with a metal lid during this storage duration (see Figure 10 right).

3.2.1 Variation in Storage Time and Conditions

Apart the variation of heating time, another study was conducted to investigate how significant the influence of storage time and storage conditions on the oxidation of a bituminous sample is.

Four binders (binder A – D) with different specification classes were investigated to determine whether different penetration graded binders, thus different viscosities, exhibit a similar oxidation rate.

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Binder was heated to approximately 180°C for 5 – 6 minutes and the samples were prepared. Samples stored in the light were covered with a glass lid that absorbed the UV light (see Figure 11 left). Samples stored in the dark were covered with a non-transparent, plastic lid to prevent any contamination from dust (see Figure 11 right).
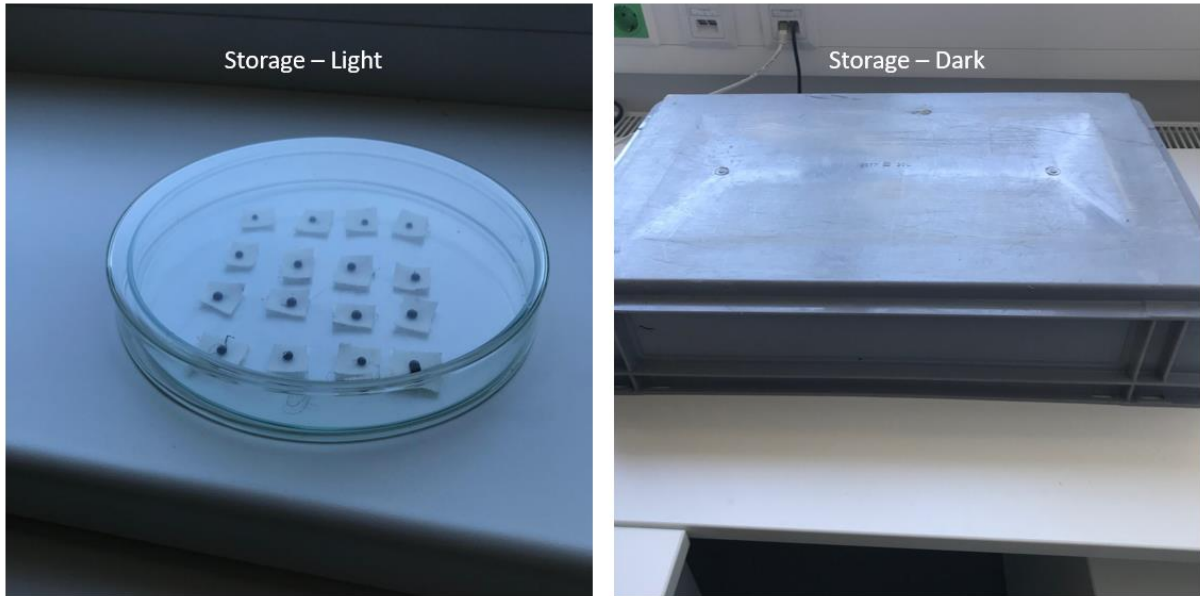

Figure 11: Samples stored in the light (left) and samples stored in the dark (right)

Samples were stored in the light and in the dark for 0, 1, 2, 3, 6, 9, 14 and 20 days. Another storage study was conducted, where the samples were stored for 0, 1, 2, 3, 4, 5, 24 and 48 hours only in the light.

3.3 Analysis Method

3.3.1 Laboratory Aging of Bitumen

RTFOT

Short-term aging was performed at laboratory with **R**olling **T**hin **F**ilm **O**ven **T**est (RTFOT) according to the EN 12607-1[7]. MATEST device type B066-01 was used to perform the STA (see Figure 12). The glass containers were filled with 35 g (+-0,5 g) bitumen and placed horizontally in the heating chamber (preheated to 163°C). RTFOT aging takes 75 minutes, and since the temperature in the chamber drops during mounting, the temperature of 163 °C should be reached within the first 15 minutes. The rotating glass containers allows the surface of the bitumen film to refresh, while a stationary metal lance blows air into it.

Figure 12: RTFOT device

PAV

Long-term aging was performed with **P**ressure **A**geing **V**essel Test (PAV) according to the EN 14679[8]. RTFOT aged binder is poured into the metal containers (50 g per container). The samples were placed in a sample holder and then transferred to the pressure vessel. Samples were exposed at 90 – 110°C and the pressure of 2,1 MPa for 20 hours. After completion of the test, the sample was placed in an oven at 163°C for 30 minutes, then collected.

Figure 13: PAV device

3.3.2 ATR-FTIR – Spectroscopy

Once the samples were prepared, they were measured using the Bruker Alpha II FTIR spectrometer (see Figure 14) equipped with a crystal diamond and a DTGS detector.

Figure 14: Bruker Alpha II FTIR spectrometer

Before the sample was placed onto the crystal for measurement, the background of the empty crystal was measured. Each sample was scanned four times in the wavenumber between 4000 cm^{-1} and 680 cm^{-1} and 24 scans. After each measurement, the crystal was cleaned with a non-toxic solvent (limonene) and a fast evaporating alcohol (isopropanol).

All spectra were recorded and processed in the attached Bruker software OPUS. After the first normalization, in which all spectra were normalized to the most intense band in the bitumen spectrum, which can be allocated to the aliphatic band at 2920 cm^{-1}, some errors were detected in the lowest intensity of the original spectrum originating from the ATR crystal, which is normally in the wavenumber of 2300cm^{-1} to 1800 cm^{-1}. To avoid this type of error, min-max normalization is required. Therefore, this normalization was performed at wavenumber of 3200 cm^{-1} to 2800 cm^{-1}.

To calculate the aging index (AI_{FTIR}), a complete integration of the baseline was needed in the three groups shown below:

After normalization, a complete integration of the baseline was performed in the three groups presented below:

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

The values obtained were calculated using Eq. 7.

$$AI_{FTIR} = \frac{AI_{CO} + AI_{SO}}{AI_{CH_3}} \tag{7}$$

One of the 16 spectra obtained per binder was chosen for plotting using OriginPro2021b. Only the fingerprint area from 1800 cm^{-1} to 680 cm^{-1} is shown in the spectra because it contains most of the bands and significant changes in the bitumen spectra.

The reason that there are many ways to evaluate the spectral data means that changing the normalization and integration method can lead to different results. By integrating the carbonyl, sulfoxide and reference aliphatic band, aging index can be calculated.

4   Results and Discussion

First, the variation of heating time of binder A – D in the unaged state will be discussed, then a comparison will be made between binder B heated in a ventilated oven, uncovered and covered with a metal lid. Furthermore, a variation of heating time and a comparison between binders from different crude oil sources but with the same specification classes (binder E and binder F) will be discussed. Then, the variation of heating time of binders A – D in the short – term aging state will be discussed. The only long-term aged binder (binder B), that is the most used in Austria, is the last binder discussed in the heating time and temperature variation study.

In addition, the study on conditions and storage time is discussed. Subject of this study are binder A – D which will be compared to each other and with RTFOT – aged binders. In addition, RTFOT+PAV – aged Binder B will be compared with binder B from storage time study.

At the end, a conclusion and recommendations are drawn.

4.1 Variation of Heating Time on the Heating Plate and in the Oven

4.1.1   Comparison of different Specification Classes from the same Crude Oil Source of unaged Bitumen

Binder A – D are from the same crude oil source and were produced in the same refinery. This means that all binders have a very similar chemical or molecular composition, thus similar FTIR spectra. However, differences in the ageing indices can be explained by differences in the polarity gradient (SARA fractions), which influence the fingerprint intensity and thus final ageing index of a binder.

The fingerprint region of the spectra of binder A heated in the heating plate is shown in Figure 15, and that of binder A heated in the ventilated oven in Figure 16.
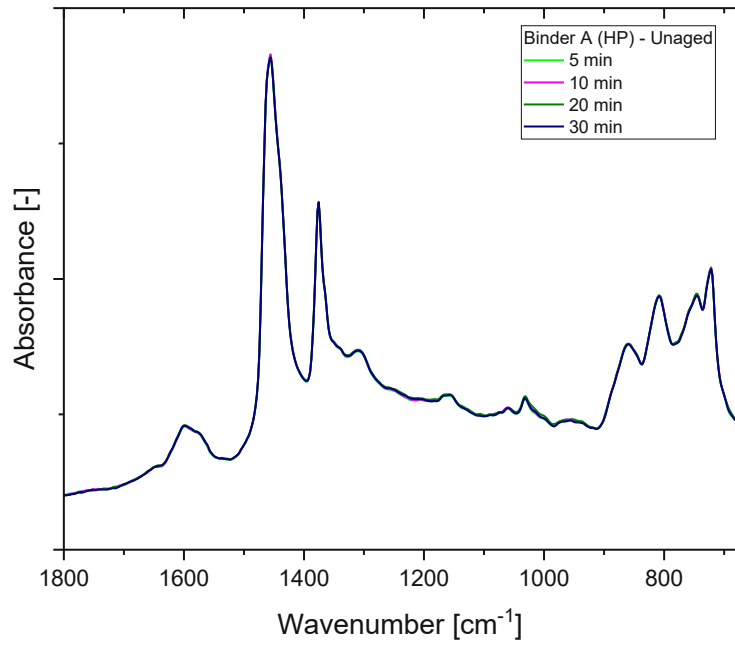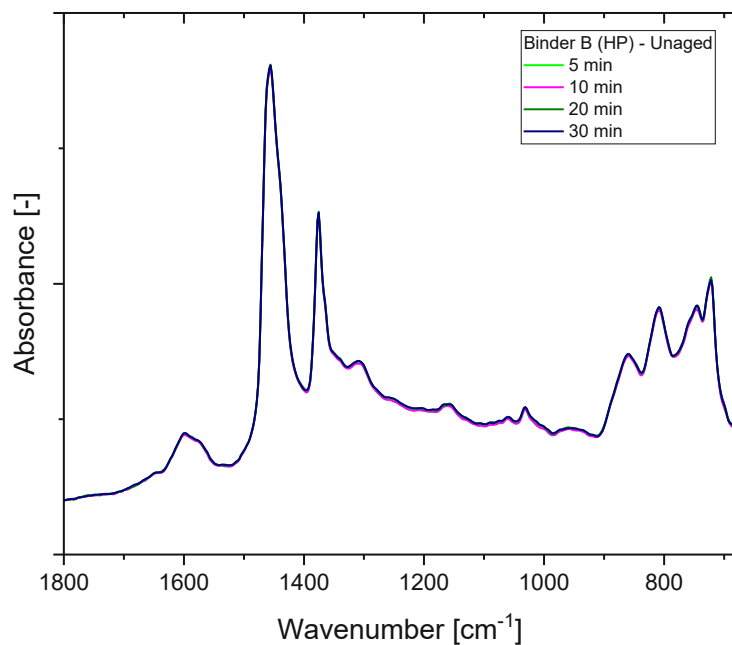
Figure 15: FTIR Spectra of unaged Binder A after 5, 10, 20 and 30 min heated on the heating plate.
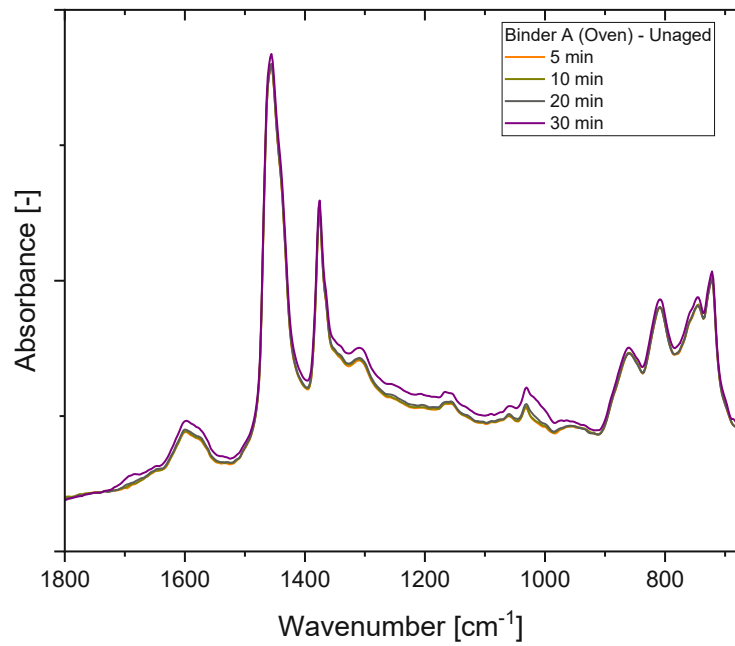
Figure 16: FTIR Spectra of unaged Binder A after 5, 10, 20 and 30 min heated in oven.

Heating binder A on the heating plate, also constantly stirring, it shows that just a small formation of sulfoxides at 1030 cm^{-1} is observed (see Figure 15). While heating the binder in an uncovered metal can in the ventilated oven, which contains 5 g of binder, causes a higher oxidation when heated for a longer time, even though the sample was not stirred while it was heating. This happens because of the hot air is blowing directly in the bitumen surface, which is around 180°C. The incensement in ketones at 1700 cm^{-1}, aromatics at 1600 cm^{-1} and sulfoxides at 1030^{-1} can be seen in Figure 16. This means that bitumen oxidizes more when in direct contact with hot air.

Figure 17 shows aging indices and standard deviation of binder A, where the difference of the binder heated in the heating plate and in the ventilated oven is obvious.
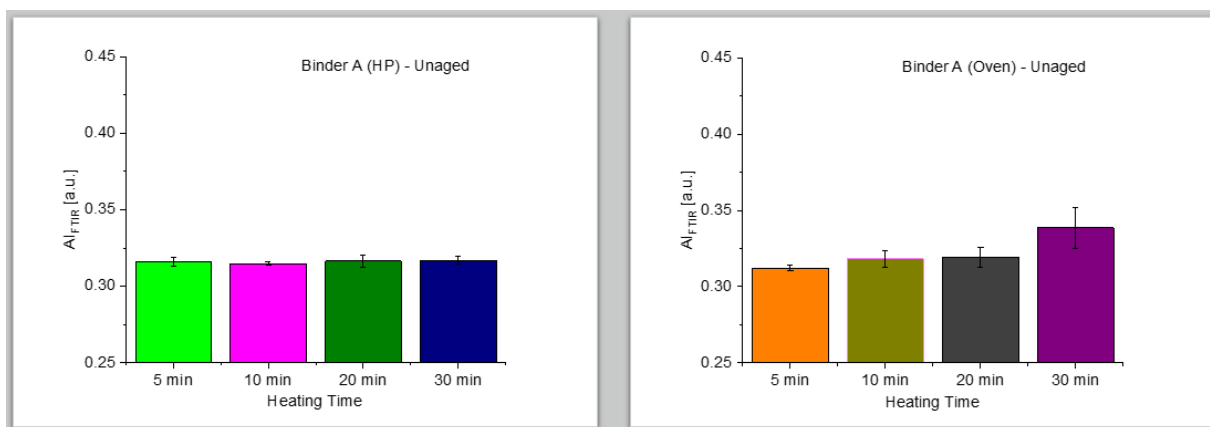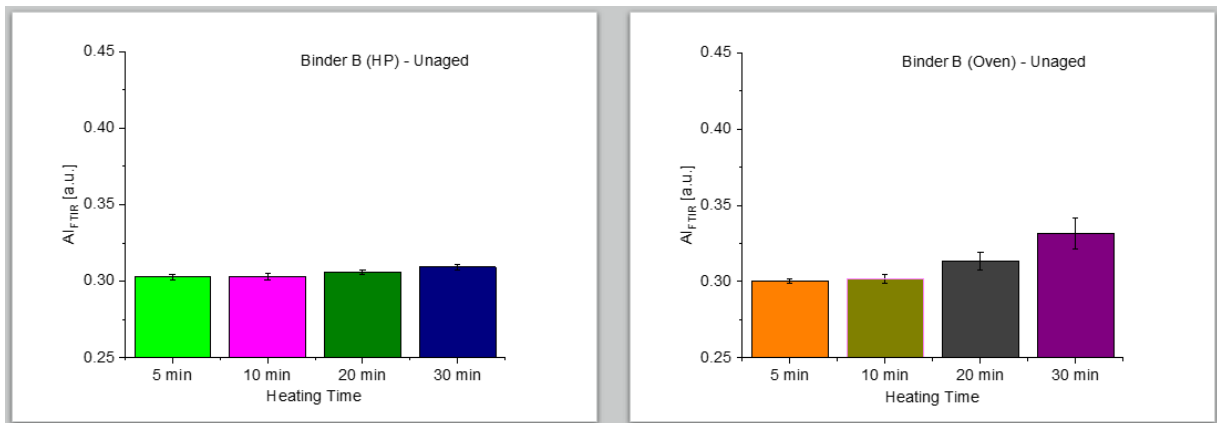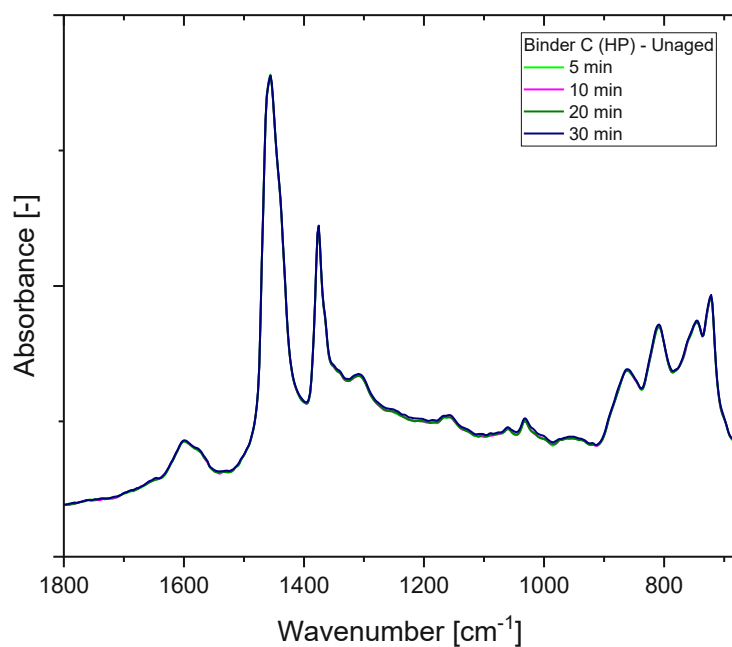

Figure 17: FTIR aging indices of unaged Binder A after 5, 10, 20 and 30 min heated on the heating plate (left) and oven (right).

In order to simplify what has been said so far, the aging indices for binder A will be presented in Table 2. The difference of aging index of Binder A between the shortest and the longest heating time when heating on the heating plate is given by Δ AI$_{FTIR}$ (5 – 30 min) = 0.001. On the other hand, when it is heated in a ventilated oven, this value is significantly higher Δ AI$_{FTIR}$ (5 – 30 min) = 0.026. As it can be seen in the Table 2, not only the oxidation trend is higher when heating the binder in the ventilated oven but also the standard deviation is also much larger. Therefore, heating the binder for a longer time in the ventilated oven means that we cannot determine its real aging index, as the ageing level can scatter much more.

Table 2: FTIR aging indices of Binder A after 5, 10, 20 and 30 min heated on the heating plate and in oven.

Heating Time		5 min	10 min	20 min	30 min	Δ (5-30 min)
Heating Plate	AI_{FTIR}	0.316	0.314	0.316	0.317	0.001
	Standard Deviation	0.003	0.0013	0.004	0.0026	
Oven	AI_{FTIR}	0.312	0.318	0.319	0.338	0.026
	Standard Deviation	0.002	0.0055	0.0066	0.0133	

A small formation of sulfoxides at 1030 cm^{-1} when heating binder B on the ventilated oven can be observed (see Figure 18). When binder B is heated in a ventilated oven for up to 20 minutes, no significant change in the FTIR spectra can be seen, as shown in Figure 19. The most significant increase in ketones at 1700 cm^{-1}, aromatics at 1600 cm^{-1} and sulfoxides at 1030^{-1} is observed when the binder is heated for longer than 20 minutes.

Figure 18: FTIR Spectra of unaged Binder B after 5, 10, 20 and 30 min heated on the heating plate.
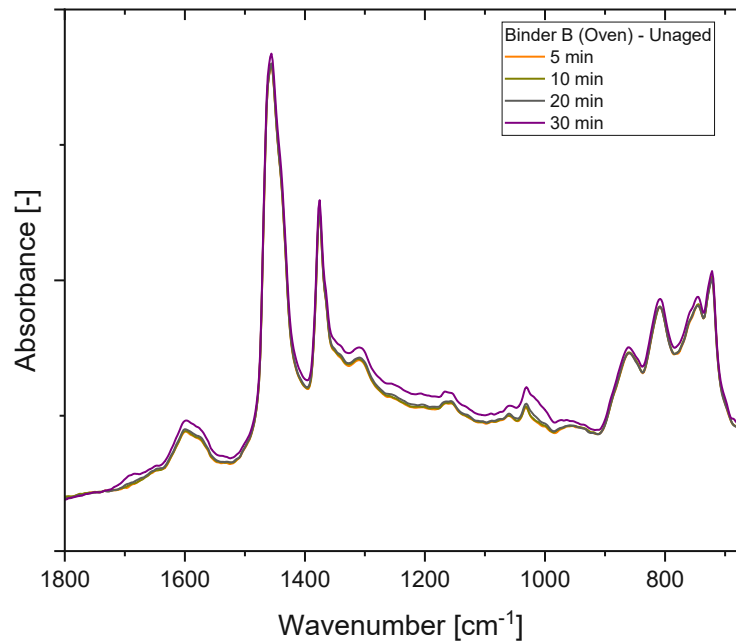
Figure 19: FTIR Spectra of unaged Binder B after 5, 10, 20 and 30 min heated in oven.

Figure 20 shows the ageing indices of Binder B, where a similar trend compared to binder A can be observed.

Figure 20: FTIR aging indices of unaged Binder B after 5, 10, 20 and 30 min heated on the heating plate (left) and oven (right).

A slight increase in the oxidation of Binder B can be seen when heating up to 30 min in the heating plate. The difference of aging index between the longest and shortest heating time of Binder B (Δ AI_{FTIR} = 0.007) is a bit higher than that of Binder A. An indicator of this may be that when dealing with softer bitumen, the aging index also increases with increase of heating time. Also, for binder B in comparison to binder A the trend of oxidation is similar. When heating

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binder B in the ventilated oven, Δ AI_{FTIR} = 0.031 is much higher than when it is heated on the heating plate, which is 0.007. Like binder A, binder B also has a high standard deviation when heated in the ventilated oven, and its actual aging index cannot be determined when heated for a longer period of time.

Table 3: FTIR aging indices of Binder B after 5, 10, 20 and 30 min heated on the heating plate and oven.

Heating Time		5 min	10 min	20 min	30 min	Δ (5-30 min)
Heating Plate	AI_{FTIR}	0.303	0.303	0.306	0.309	0.007
	Standard Deviation	0.0017	0.0022	0.0013	0.0019	
Oven	AI_{FTIR}	0.300	0.302	0.313	0.332	0.031
	Standard Deviation	0.0013	0.0029	0.0056	0.0103	

Since the fingerprint region of the spectra of the next two binders to be presented is very similar to the two presented previously, the FTIR spectra will not be discussed, but only shown. FTIR spectra of binder C heated on the heating plate and on the ventilated oven are shown in Figure 21 and Figure 22.

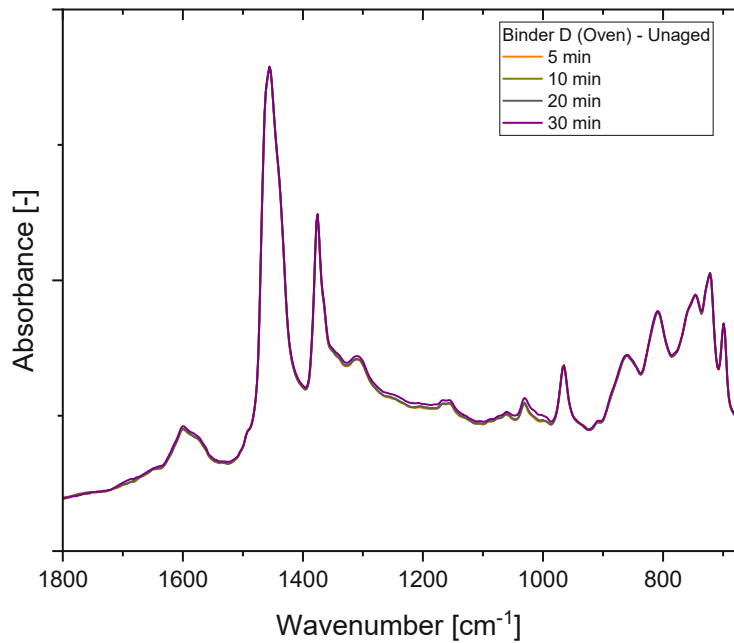*Figure 21: FTIR Spectra of unaged Binder C after 5, 10, 20 and 30 min heated on the heating plate.*
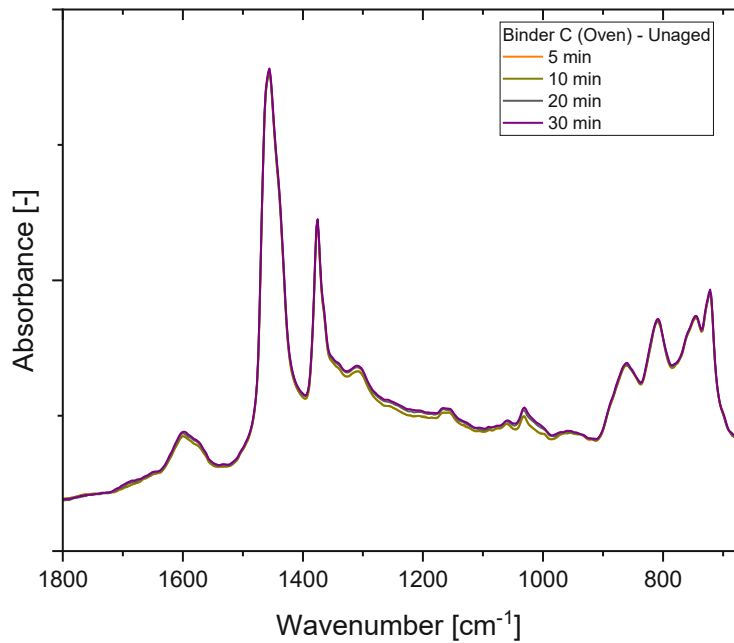
Figure 22: FTIR Spectra of unaged Binder C after 5, 10, 20 and 30 min heated in the ventilated oven.

Aging indices of the softest binder (160/220) from all four heating times are shown in the Figure 23 and in numerical values in the Table 4. As mentioned before, as the softness of the binder increases, the aging indices increase too. Δ AI_{FTIR} (5-30 mins) for binder C when heating in the heating plate (0.008) is much lower than Δ AI_{FTIR} (5-30 mins) in the ventilated oven (0.028).
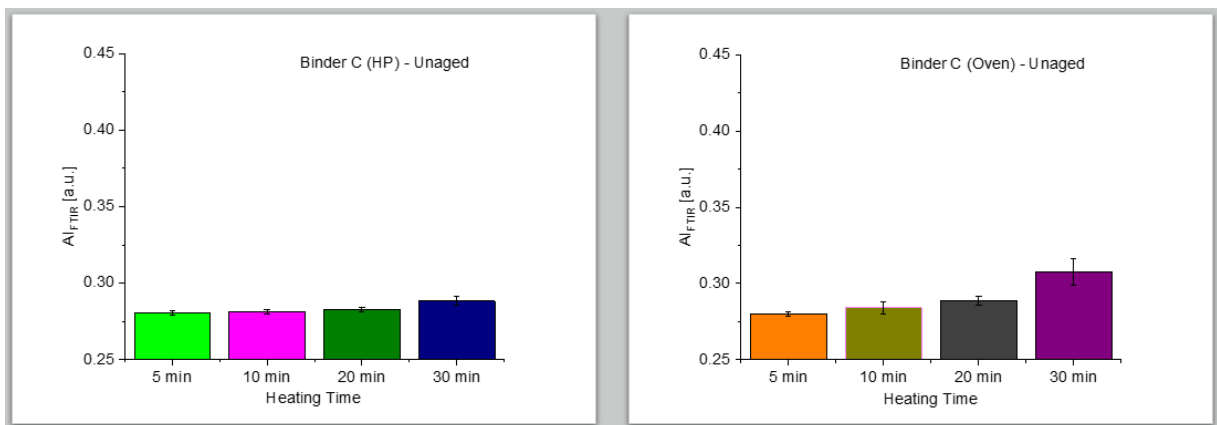
Figure 23: FTIR aging indices of unaged Binder C after 5, 10, 20 and 30 min heated on the heating plate (left) and oven (right).

Here, too, it is shown that heating the binder for a longer time in the ventilated oven can lead to very high oxidation and large standard deviation, so that here, too, heating the binder for a longer time in the ventilated oven is not recommended.

Table 4: FTIR aging indices of Binder C after 5, 10, 20 and 30 min heated on the heating plate and oven.

Heating Time		5 min	10 min	20 min	30 min	Δ (5-30 min)
Heating Plate	AI_{FTIR}	0.280	0.281	0.283	0.288	0.008
	Standard Deviation	0.0014	0.0016	0.0015	0.0027	
Oven	AI_{FTIR}	0.280	0.284	0.289	0.308	0.028
	Standard Deviation	0.0014	0.0041	0.003	0.0089	

Figure 24 shows the FTIR spectra of the binder heated in the heating plate, where Figure 25 shows that of binder A heated in the ventilated oven. The difference in the FTIR spectra compared to three other binders is at 966 and 699 cm^{-1}, which represents the modification of the binder D.
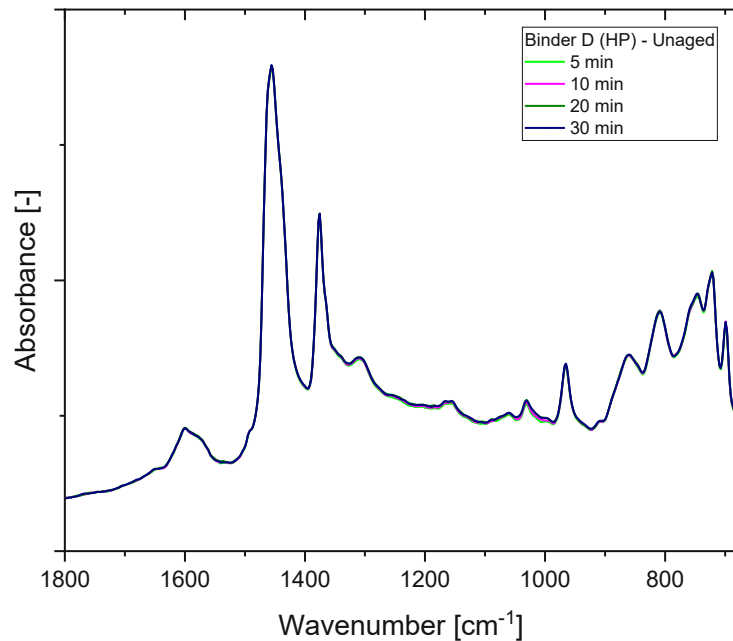
Figure 24: FTIR Spectra of unaged Binder D after 5, 10, 20 and 30 min heated on the heating plate.

Figure 25: FTIR Spectra of unaged Binder D after 5, 10, 20 and 30 min heated in the ventilated oven.

Binder D is the last of the four binders from the same crude source investigated in this study. Binder B is the base bitumen of binder D, which is a polymer-modified bitumen. The reason for this investigation was to find out whether a PmB is more or less sensitive than its unmodified base bitumen, binder B, when heated on the heating plate and in the ventilated oven. A PmB is more difficult to process since its properties change drastically due to the addition of the polymer. Therefore, another reason for this investigation was to find out whether the heating time was sufficient to reach the workable state. Aging indices and standard deviations of binder D are shown in the Figure 26 and the similarities with binder B (see Figure 26 and Figure 20), especially when the binder is heated on the heating plate, can be seen.
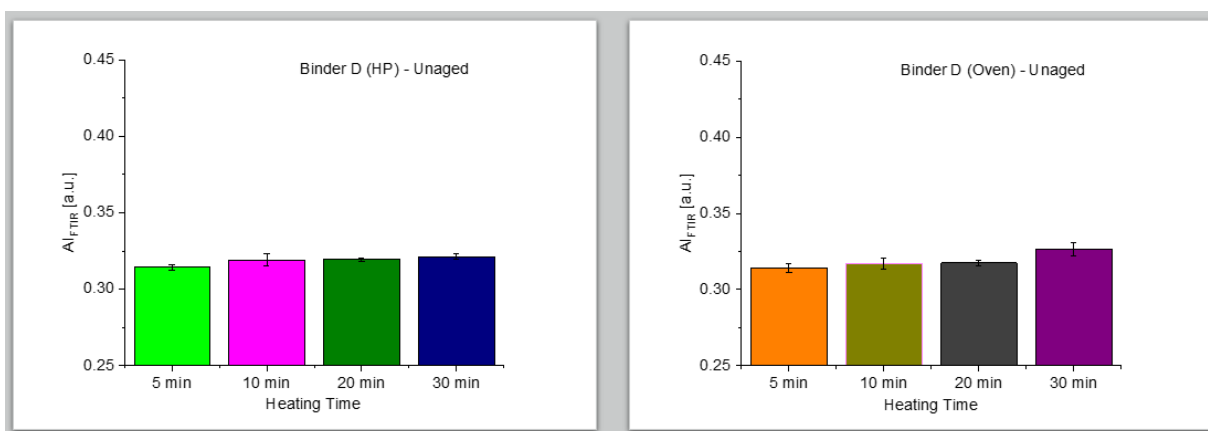
Figure 26: FTIR aging indices of unaged Binder D after 5, 10, 20 and 30 min heated on the heating plate (left) and oven (right).

Comparing the data of Table 5 and Table 3, it can be seen that Δ AI$_{FTIR}$ (5-30 mins) of PmB has the same value as its base unmodified bitumen (binder B) 0.007, when the binder was heated on the heating plate. Nevertheless, when the binder was heated in the ventilated oven, where Δ AI$_{FTIR}$ (5-30 min) of binder D is 0.012, which is much smaller than Δ AI$_{FTIR}$ (5-30 min) of its unmodified base bitumen (binder B) 0.031.

Table 5: FTIR aging indices of Binder D after 5, 10, 20 and 30 min heated on the heating plate and oven.

Heating Time		5 min	10 min	20 min	30 min	Δ (5-30 min)
Heating Plate	AI$_{FTIR}$	0.314	0.319	0.319	0.321	0.007
	Standard Deviation	0.0018	0.0038	0.0011	0.0017	
Oven	AI$_{FTIR}$	0.314	0.317	0.318	0.327	0.012
	Standard Deviation	0.0035	0.0035	0.0020	0.0042	

Based on the data in Table 4 and during the practical work when the samples were prepared, it can be assumed that the heating time was sufficient to bring PmB to a good workable state. Furthermore, the overall thermal ageing susceptibility seems to be lower, when comparing the oxidation behavior in the oven. This can be explained by the addition of the polymer, which makes the PmB more robust to such thermal stress.

From the results of all binders, it will be recommended that the standard deviation of binder oxidation should not exceed the value of 0.005 and to pay attention of the homogeneity in order to obtain more meaningful aging indices. Homogeneity or lower standard deviation has

been seen in samples prepared in the heating plate, while the opposite has happened when samples were prepared in the ventilated oven, since stirring in the oven was not possible.

From the data collected so far, it can be concluded that the maximum heating time for all binders heated on the heating plate is 5 to 20 minutes, except for binder A, which can be heated for up to 30 minutes, while the heating time for binders heated in the ventilated oven is a maximum of 5 to 10 minutes. However, since all binders reach the workable state after 5 minutes, it is recommended a heating time for all binders for a maximum of 5 to 10 minutes in order to induce the least oxidation possible but ensure proper homogenization.

4.1.2   Comparison of Binder B uncovered and covered with a Metal Lid when heated in the Oven

As seen before, heating a small amount of binder in a ventilated oven for a longer time (up to 30 minutes in this case) can cause a high oxidation rate of the binder and reduce repeatability significantly (broadening of the standard deviation). This is due to the direct contact of hot air with the bitumen surface. For this reason, another study was conducted in which the binder was heated in a ventilated oven, but now in a metal can that was covered with a metal lid in order to prevent hot air from being blown directly onto the surface of the binder. Binder B was used for this study because it exhibits the highest oxidation rate when it was placed in an uncovered metal can and heated in the ventilated oven.

Figure 27 shows fingerprint region of the spectra of binder B heated on the ventilated oven (covered) and as one can see, no significant changes in the spectra can be observed.
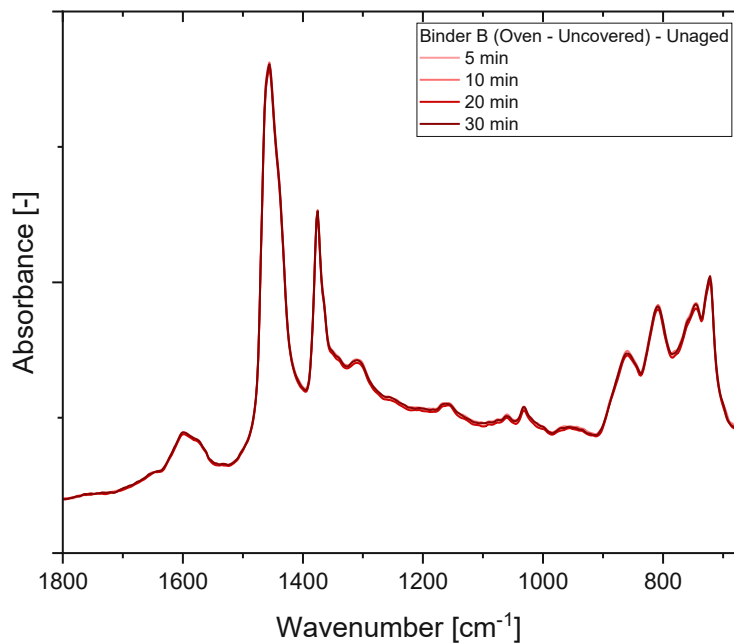
Figure 27: FTIR Spectra of unaged Binder B after 5, 10, 20 and 30 min heated in the ventilated oven (covered).

The comparison of aging indices between heating plate, covered and uncovered metal can in ventilated oven is shown in the Figure 28.
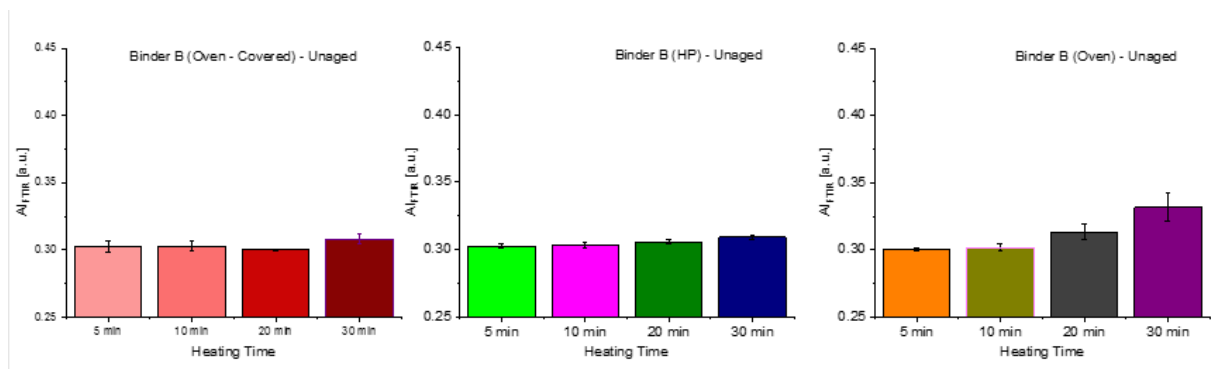
Figure 28: FTIR aging indices of unaged Binder B after 5, 10, 20 and 30 min heated covered in the ventilated oven (left), on the heating plate (middle) and uncovered in the ventilated oven (right).

It is clear from the graph that covering the metal can with a lid results in a much lower oxidation level of the binder, compared to heating it in an open metal can.

From Table 6 it can be seen that the results are much better in comparison to the open metal can but also in regard to the results from the heating plate, as Δ AI_{FTIR} (5 − 30 min) shows a value of 0.005.

Table 6: FTIR aging indices of Binder B after 5, 10, 20 and 30 min heated on the heating plate and oven (uncovered and covered).

Heating Time		5 min	10 min	20 min	30 min	Δ (5-30 min)
Heating Plate	AI_{FTIR}	0.303	0.303	0.306	0.309	0.007
	Standard Deviation	0.0017	0.0022	0.0013	0.0019	
Oven	AI_{FTIR}	0.300	0.302	0.313	0.332	0.031
	Standard Deviation	0.0013	0.0029	0.0056	0.0103	
Oven (Covered)	AI_{FTIR}	0.303	0.303	0.300	0.308	0.005
	Standard Deviation	0.0044	0.0031	0.0007	0.0036	

The disadvantage of heating a closed metal can in a ventilated oven is that when the can must be removed from the oven, it must be opened quickly to prepare the samples while the bitumen is still hot. Because the can is small and hot, this process can take some time, and thick gloves must be worn to avoid injury when removing the lid.

4.1.3 Comparison of same Specification Classes from the different Crude Oil Source of unaged Bitumen

As mentioned in Chapter 3.1, the first four binders were from the same oil source and the last two, binder E and binder F, were from two other crude oil sources that were subjected to thermal exposure at the same temperature and duration in order to expand the information on this subject and to investigate how binders with the same penetration grade but from different crude oil sources behave. Since heating the binders in a ventilated oven causes severe oxidation, it was decided for this study to test these two binders covered with a metal lid while they were heated in the oven.

Just a small formation of sulfoxides at 1030 cm^{-1} can be observed when looking at fingerprint region of the spectra of binder E heated on the heating plate (see Figure 29). A slightly higher formation of sulfoxides and carbonyls occurs when heating binder E in the ventilated oven (see Figure 30).
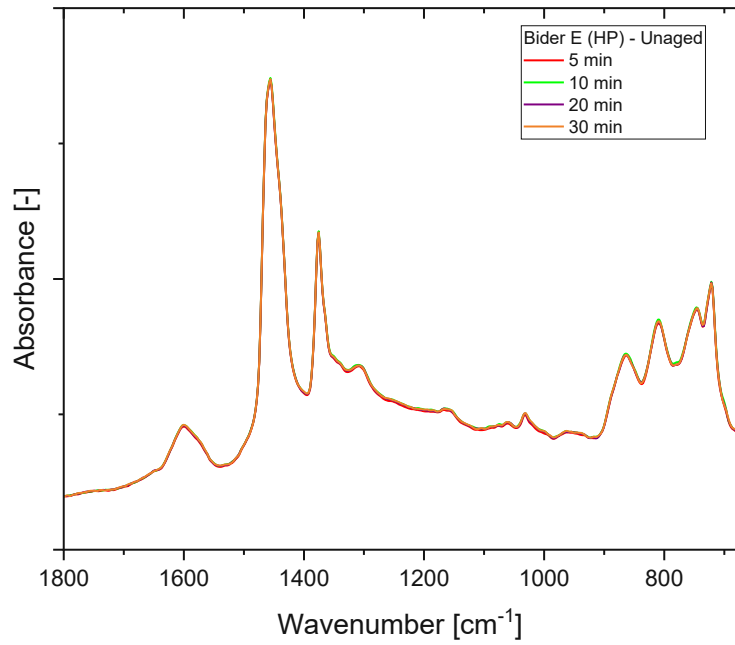
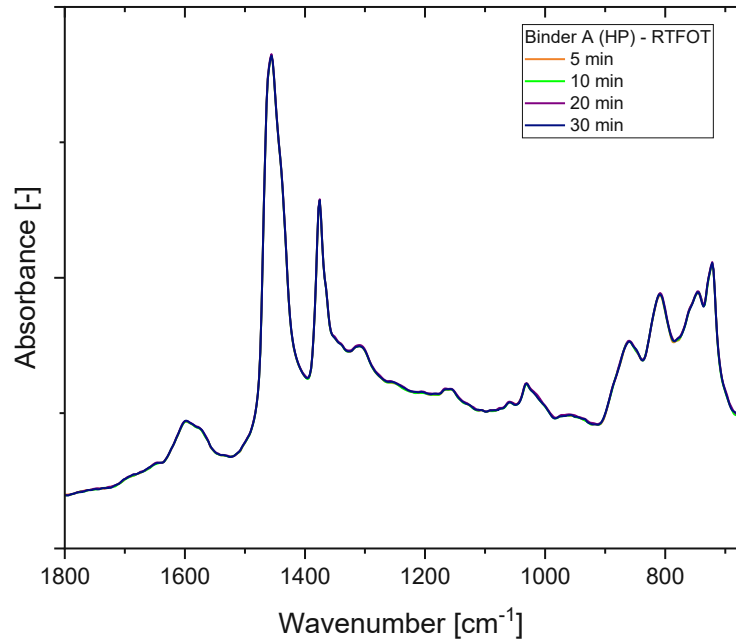*Figure 29: FTIR Spectra of unaged Binder E after 5, 10, 20 and 30 min heated on the heating plate.*
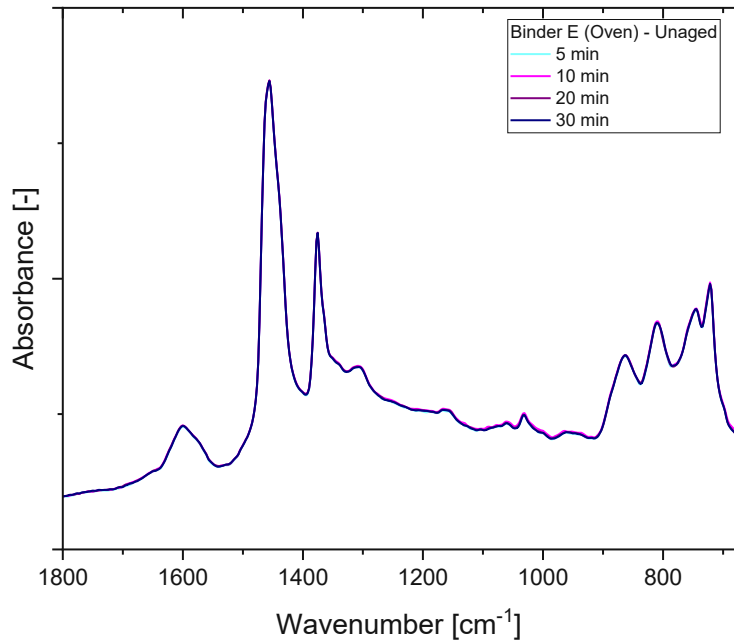
Figure 30: FTIR Spectra of unaged Binder E after 5, 10, 20 and 30 min heated in the ventilated oven.

Although binder E was covered with a metal lid during heating in the ventilated oven, this could not prevent it from reaching a higher oxidation, as showed in Figure 31, than when heated in the heating plate.
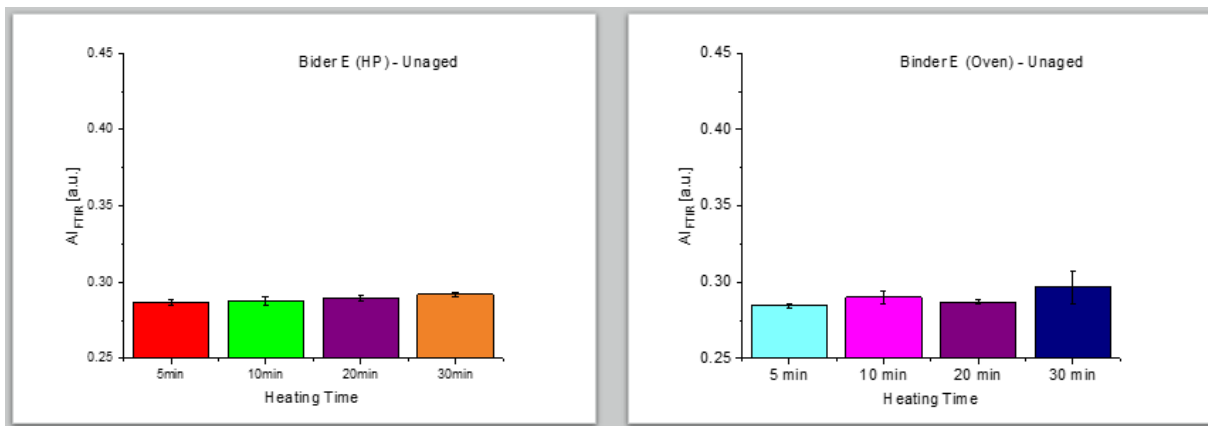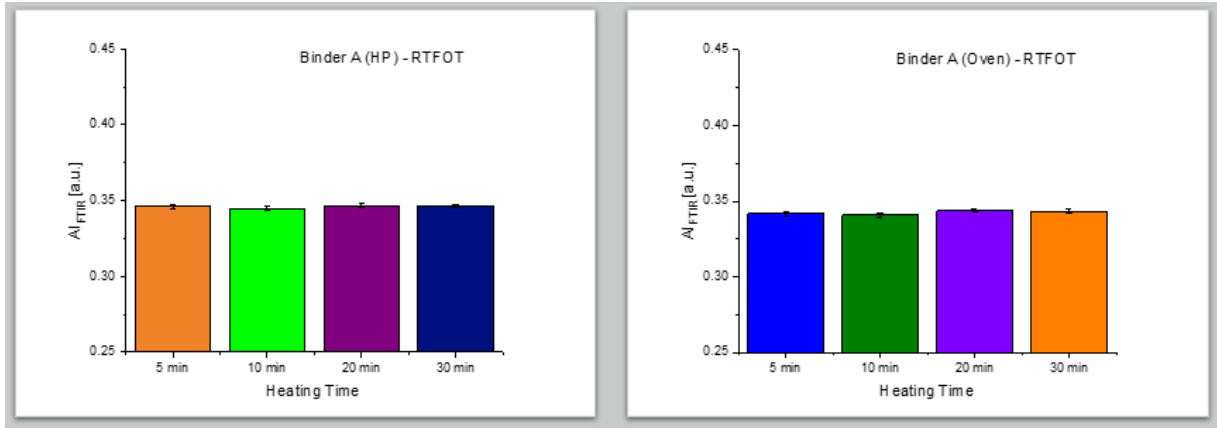

Figure 31: FTIR aging indices of unaged Binder E after 5, 10, 20 and 30 min heated on the heating plate (left) and oven (right).

Comparing binder E with covered binder B (see Table 6 and Table 7), it can be seen that binder E has a higher standard deviation and larger difference of oxidation level. While Δ AI_{FTIR} (5 − 30 mins) of binder B doesn't exceed the recommended value (0.005), Δ AI_{FTIR} (5 − 30 mins) of binder E is much higher (0.012).

Table 7: FTIR aging indices of unaged Binder E after 5, 10, 20 and 30 min heated on the heating plate and oven.

Heating Time		5 min	10 min	20 min	30 min	Δ (5-30 min)
Heating Plate	AI_{FTIR}	0.287	0.288	0.290	0.292	0.005
	Standard Deviation	0.0020	0.0028	0.0016	0.0011	
Oven	AI_{FTIR}	0.285	0.290	0.287	0.297	0.012
	Standard Deviation	0.0011	0.0042	0.0013	0.011	

On the other hand, standard deviation and oxidation is under the recommended values when heating binder E on the heating plate.

Figure 32 and Figure 33 show that the fingerprint region of the spectra of binder F heated on the heating plate and in the ventilated oven is almost identical.
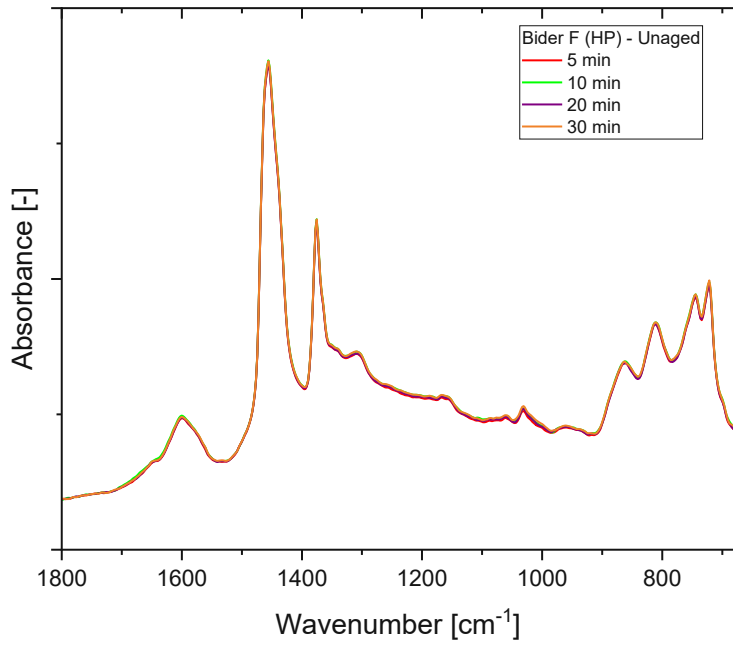
Figure 32: FTIR Spectra of unaged Binder F after 5, 10, 20 and 30 min heated on the heating plate.
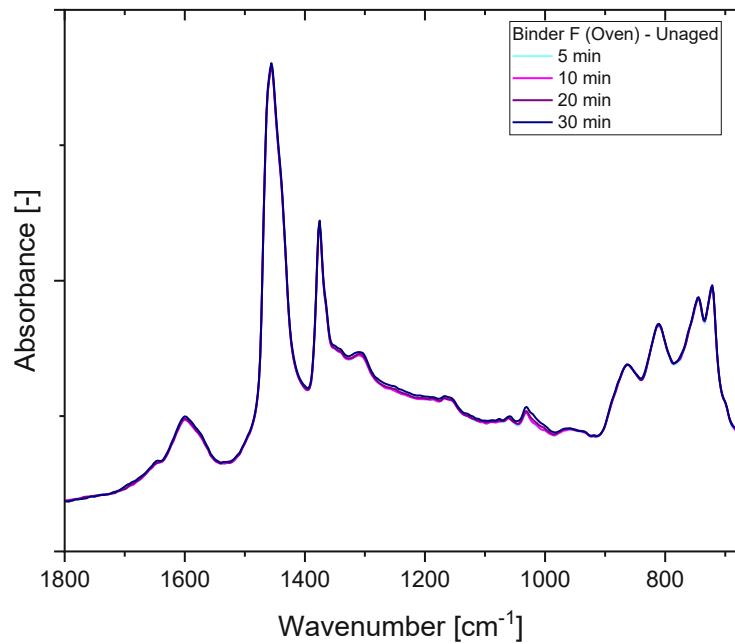
Figure 33: FTIR Spectra of unaged Binder F after 5, 10, 20 and 30 min heated in the ventilated oven.

Binder F exhibits more similarities with binder B, with both having lower aging indices when heated in the ventilated oven than in the heating plate (see Figure 34 and Figure 28).

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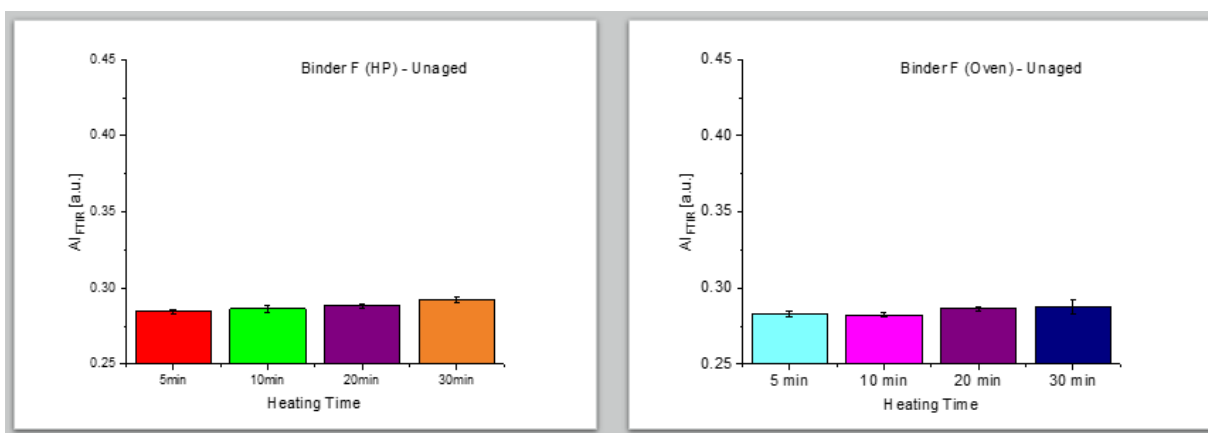
Figure 34: FTIR aging indices of unaged Binder F after 5, 10, 20 and 30 min heated on the heating plate (left) and oven (right).

As shown in the Table 8, difference of oxidation level Δ AI_{FTIR} (5 – 30 mins) of binder F (0.008) when heated on the heating plate is a bit higher than Δ AI_{FTIR} (5 – 30 mins) when heated in the ventilated oven (0,004).

Table 8: FTIR aging indices of unaged Binder F after 5, 10, 20 and 30 min heated on the heating plate and oven.

Heating Time		5 min	10 min	20 min	30 min	Δ (5-30 min)
Heating Plate	AI_{FTIR}	0.284	0.286	0.288	0.292	0.008
	Standard Deviation	0.0020	0.0028	0.0016	0.0011	
Oven	AI_{FTIR}	0.283	0.283	0.286	0.287	0.004
	Standard Deviation	0.0018	0.0016	0.0014	0.005	

Although these two binders don't show a significant oxidation rate or large standard deviation, even when heated for up to 30 minutes (except binder E heated in the oven at 30 min), a maximum heating time of 5 – 10 minutes is recommended.

4.2 Comparison of different Specification Classes from the same Crude Oil Source of Short-Term Aged Bitumen

As mentioned in the chapter 2.5.1, short-term aging was performed at laboratory with Rolling Thin Film Oven Test (RTFOT) according to the EN 12607 – 1. Samples from RTFOT – aged binder were prepared at the same temperature (180 °C) and for the same duration (up to 30 minutes) as the samples that were prepared from unaged binder on the heating plate and in the ventilated oven.

The fingerprint region of the spectra of RTFOT – aged binder A heated in the heating plate or in the ventilated oven for up to 30 minutes shows that almost no formation of carbonyls and sulfoxides occurs (see Figure 35 and Figure 36).

Figure 35: FTIR Spectra of RTFOT – aged Binder A after 5, 10, 20 and 30 min heated on the heating plate.
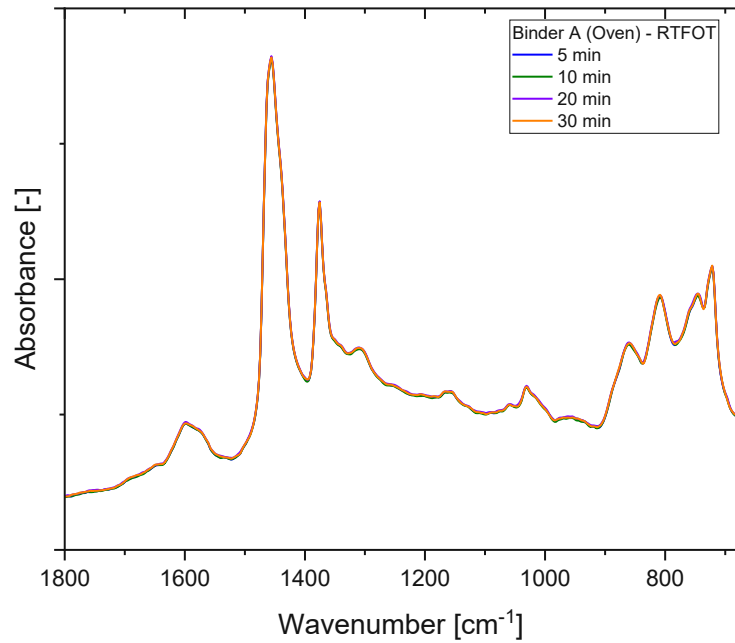
Figure 36: FTIR Spectra of RTFOT – aged Binder A after 5, 10, 20 and 30 min heated in the ventilated oven

A comparison between unaged and RTFOT – aged binder will be made bellow. Aging indices of RFTOT – aged binder A are shown in Figure 37.

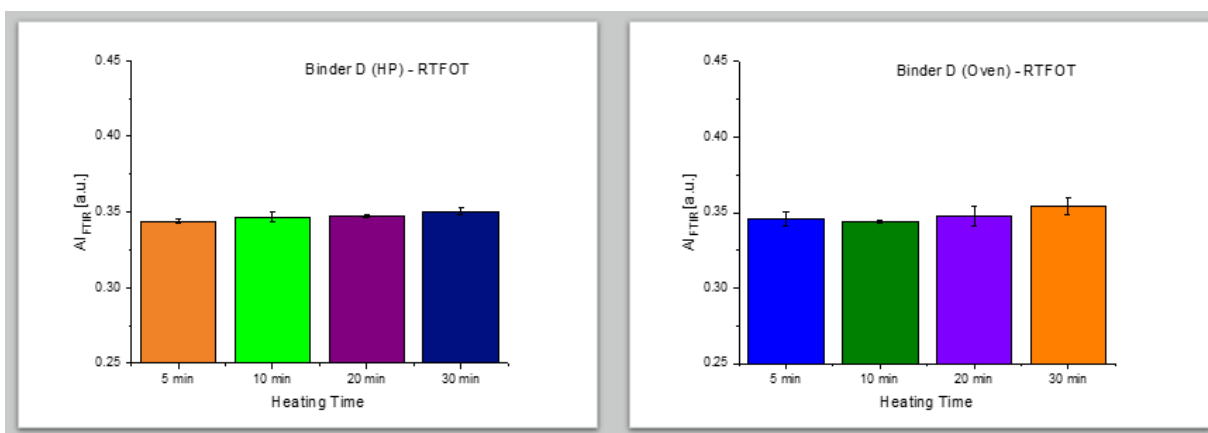*Figure 37: FTIR aging indices of RTFOT – aged Binder A after 5, 10, 20 and 30 min heated on the heating plate (left) and oven (right).*

Looking at the aging indices and standard deviation (see Table 9) shows that RTFOT – aged binder A heated for up to 30 minutes does not oxidize much. Δ AI_{FTIR} (5-30 min) for binder A when heated on heating plate is (0.0003), which is lower than when the binder is heated in ventilated oven (0.0014). However, both of them are under the recommended value (0.005). On the other hand, it is interesting to note here that the binder heated in the ventilated oven is less oxidized than that heated in the heating plate, even though hot air blows direct into the binder surface when heated in the ventilated oven.

Table 9: FTIR aging indices of RTFOT – aged Binder A after 5, 10, 20 and 30 min heated on the heating plate and oven.

Heating Time		5 min	10 min	20 min	30 min	Δ (5-30 min)
Heating Plate	AI_{FTIR}	0.346	0.345	0.346	0.346	0.0003
	Standard Deviation	0.0016	0.0014	0.0013	0.0012	
Oven	AI_{FTIR}	0.342	0.341	0.344	0.343	0.0014
	Standard Deviation	0.0013	0.0015	0.0012	0.0015	

Comparing unaged binder A to the RTFOT – aged binder A, it can be seen that aging after heating the binder in the heating plate reaches the aging index of 0.316, respectively 0.346 Thus, the difference between aging index of unaged binder A and an RTFOT – aged binder A is 0.03, which means that an increase of 0.03 in the aging index results in the unaged binder reaching the RTOFT aging state. Table 2 shows that when the unaged binder A is heated in the

ventilated oven, Δ AI_{FTIR} (5-30 min) is (0.026), which means that it almost reaches the RTFOT – aging state.

In the following, only the aging indices of binders B, C and D will be briefly presented, since the spectra do not differ significantly from each other.

A comparison of RTFOT – aged binder B heated in the heating plate and ventilated oven is shown in Figure 38. Here, it can be seen, that the RTFOT-aged binder is not very sensitive to thermal stresses even when heated for up to 30 minutes.
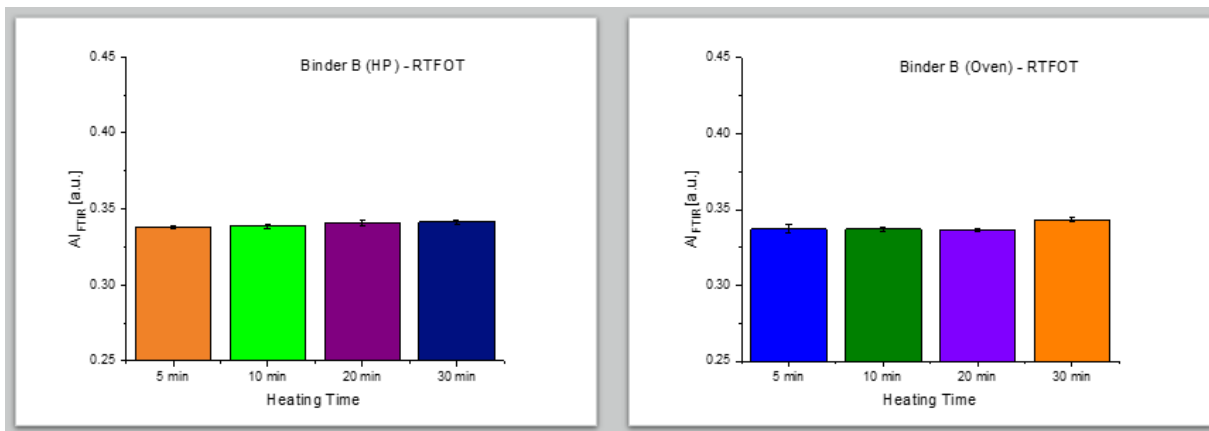
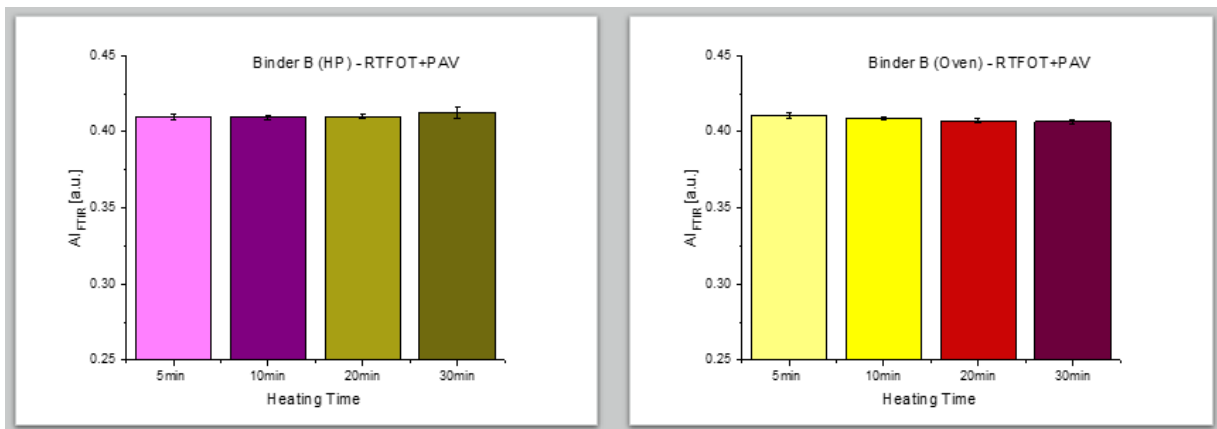Figure 38: FTIR aging indices of RTFOT – aged Binder B after 5, 10, 20 and 30 min heated on the heating plate (left) and oven (right).

The difference of the aging indices for the samples prepared in the heating plate and those in the ventilated oven is very small, however Δ AI_{FTIR} (5-30 min) for binder heated in the ventilated oven (0.006) (see Table 10) exceed the recommended value (0.005).

Table 10: FTIR aging indices of RTFOT – aged Binder B after 5, 10, 20 and 30 min heated on the heating plate and oven.

Heating Time		5 min	10 min	20 min	30 min	Δ (5-30 min)
Heating Plate	AI_{FTIR}	0.338	0.339	0.341	0.342	0.003
	Standard Deviation	0.0011	0.0016	0.0015	0.0012	
Oven	AI_{FTIR}	0.337	0.337	0.337	0.343	0.006
	Standard Deviation	0.0027	0.0015	0.0009	0.0015	

As the results have shown for the past two examined binders that they didn't oxidize much while exposed to thermal stress for up to 30 minutes, Figure 39 shows that also RTFOT – aged binder C has almost the same trend.
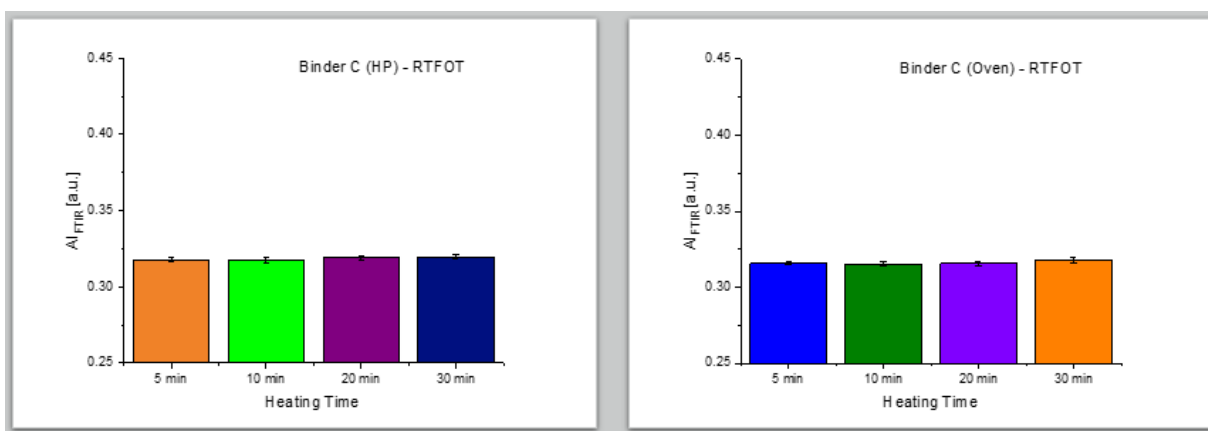
Figure 39: FTIR aging indices of RTFOT – aged Binder C after 5, 10, 20 and 30 min heated on the heating plate (left) and oven (right).

Similarities of binder C and binder A are as follows: both binders oxidize more when heated in the heating plate (see Table 11 and Table 9). Regardless of the device in which binder C is heated, Δ AI_{FTIR} (5-30 min) is same (0.002), as shown in Table 11, and it is below the recommended value (0.005). Standard deviation is relatively low for both heating devices too, which confirms good repeatability.

Table 11: FTIR aging indices of RTFOT – aged Binder C after 5, 10, 20 and 30 min heated on the heating plate and oven.

Heating Time		5 min	10 min	20 min	30 min	Δ (5-30 min)
Heating	AI_{FTIR}	0.318	0.317	0.319	0.320	0.002
Plate	Standard Deviation	0.0016	0.0017	0.0001	0.0013	
Oven	AI_{FTIR}	0.316	0.316	O.316	0.318	0.002
	Standard Deviation	0.0009	0.0017	0.0013	0.0018	

Furthermore, RTFOT – aged binder D (see Figure 40) has a higher standard deviation when heated in the ventilated oven but not when heated in the heating plate. As mentioned before, binder D is a polymer-modified binder, for which is more difficult to achieve a workable state; it has also become stiffer due to aging, which could be the reason for the higher standard deviation.

Figure 40: FTIR aging indices of RTFOT – aged Binder D after 5, 10, 20 and 30 min heated on the heating plate (left) and oven (right).

There is not a big difference between Δ AI_{FTIR} (5-30 min) (see Table 12), when the binder is heated in the heating plate (0.006), which is a bit lower than Δ AI_{FTIR} (5-30 min) of the binder heated in the ventilated oven (0.008). Although both of them are above 0.005, therefore it is not recommended to heat them longer than 20 minutes.

Table 12: FTIR aging indices of RTFOT – aged Binder D after 5, 10, 20 and 30 min heated on the heating plate and oven.

Heating Time		5 min	10 min	20 min	30 min	Δ (5-30 min)
Heating Plate	AI_{FTIR}	0.344	0.347	0.347	0.350	0.006
	Standard Deviation	0.0013	0.0031	0.0008	0.0022	
Oven	AI_{FTIR}	0.346	0.344	0.348	0.354	0.008
	Standard Deviation	0.0044	0.0011	0.0068	0.0054	

From the data collected, it can be seen in the Table 8, Table 9, Table 10 and Table 11 that heating the RTFOT – aged binder on the heating plate and in the ventilated oven for up to 30 minutes leads to a very small increase of the aging index. Overall, standard deviations are small and difference of the oxidation level Δ AIFTIR (5-30 min) does not exceed the recommended value (0.005) except for binder D, which shows a higher standard deviation and a slightly higher difference of the aging index. Thus, it can be concluded that the oxidation of the binder after short-term aging is not significantly affected by heat exposure.

4.3 Comparison of different Specification Classes from the same Crude Oil Source of Long-Term Aged Bitumen

Although it was shown in the previous chapter that for binders that have been short – term aged, heat exposure does not have a significant influence on their oxidation, nevertheless another study was carried out with a binder that has been long – term aged (RTFOT+PAV), to see whether RTFOT+PAV – aged binder is sensitive to thermal exposure or not. Binder B was selected for this study, since it is the most common type of binder used in Austria. Spectra of RTFOT+PAV – aged binder B heated on the heating plate (see Figure 41) and in the ventilated oven (see Figure 42) proves the expectation that the sensitivity to heat exposure has dropped.
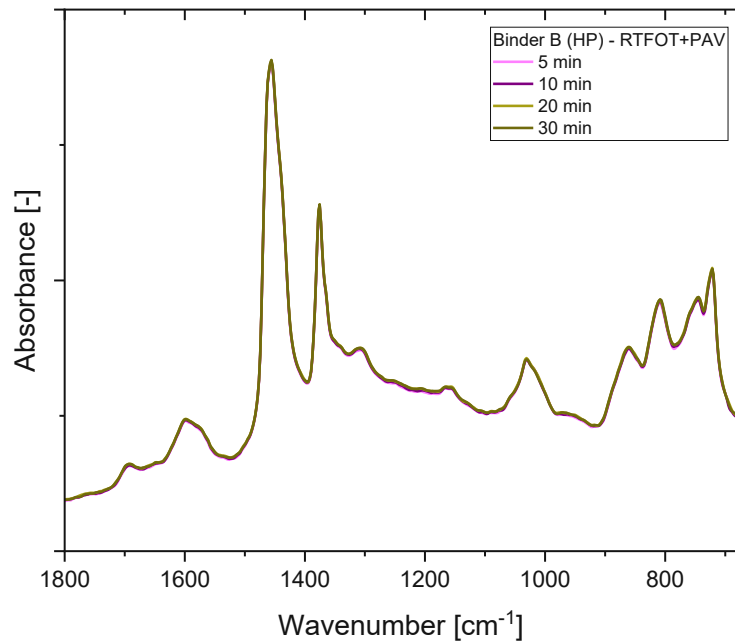
Figure 41: FTIR Spectra of RTFOT+PAV – aged Binder B after 5, 10, 20 and 30 min heated on the heating plate.
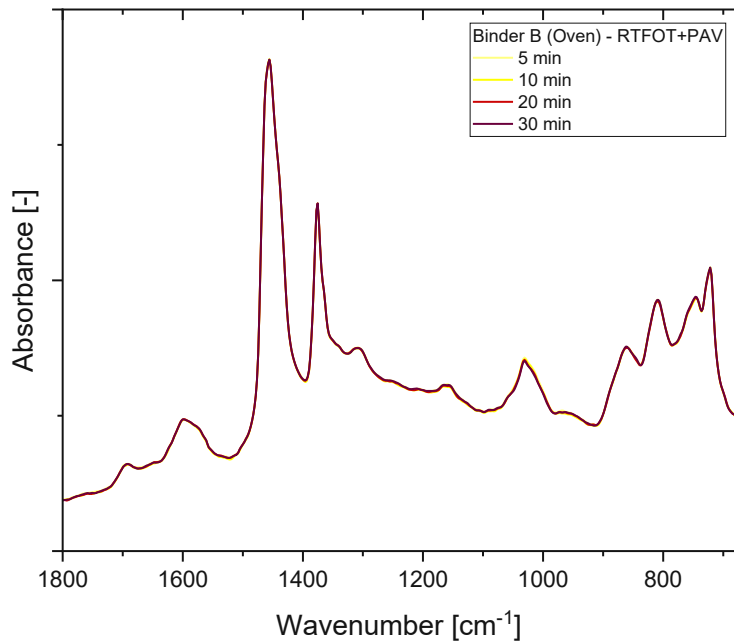
Figure 42: FTIR Spectra of RTFOT+PAV – aged Binder B after 5, 10, 20 and 30 min heated in the ventilated oven

Its aging indices and comparison between heating plate and ventilated oven are shown in Figure 43.

Figure 43: FTIR aging indices of RTFOT+PAV – aged Binder B after 5, 10, 20 and 30 min heated on the heating plate (left) and oven (right).

The difference of aging index level (see Table 13) when the binder is heated on the heating plate Δ AI_{FTIR} (5-30 min) is (0.003) and when it is heated in the ventilated oven is (0.004), with both of them under recommended value (0.005) , which means that heating long – term aged binder for a longer time does not cause a high oxidation.

Table 13: FTIR aging indices of RTFOT+PAV – aged Binder D after 5, 10, 20 and 30 min heated on the heating plate and oven.

Heating Time		5 min	10 min	20 min	30 min	Δ (5-30 min)
Heating Plate	AI$_{FTIR}$	0.410	0.409	0.410	0.412	0.003
	Standard Deviation	0.0022	0.0014	0.0013	0.0034	
Oven	AI$_{FTIR}$	0.410	0.409	0.407	0.407	0.004
	Standard Deviation	0.0018	0.0013	0.0015	0.0013	

The standard deviation is also very low for both heating devices. Thus, it can be concluded from the collected data (see Table 13) that RTFOT+PAV aged binder is not sensitive to heat exposure while heating it for up to 30 minutes. However, since the study was conducted with only one binder, further studies with other binders are required.

5 Variation in Storage Time and Conditions

Since FTIR spectroscopy measures only few micrometers of the sample's surface, storage time and conditions are from a great importance. Thus, because the surface of the binder is very sensitive too, the results below will show how the samples behaved when they are exposed to a visible light or covered with a plastic lid to prevent light from reaching the binder surface. Fingerprint area of the spectra of binder A – D (see Figure 44) shows an increase in the carbonyl – band (1660 – 1800 cm^{-1}), sulfoxide – band (1079 – 984 cm^{-1}) and aliphatic – band (1525 – 1350 cm^{-1}) after storing binders in the light. In addition, an overall intensity increase can be observed (see Figure 44). This overall intensity increase can be linked with an increase in the polarity of the material, which was shown in previous work [12].
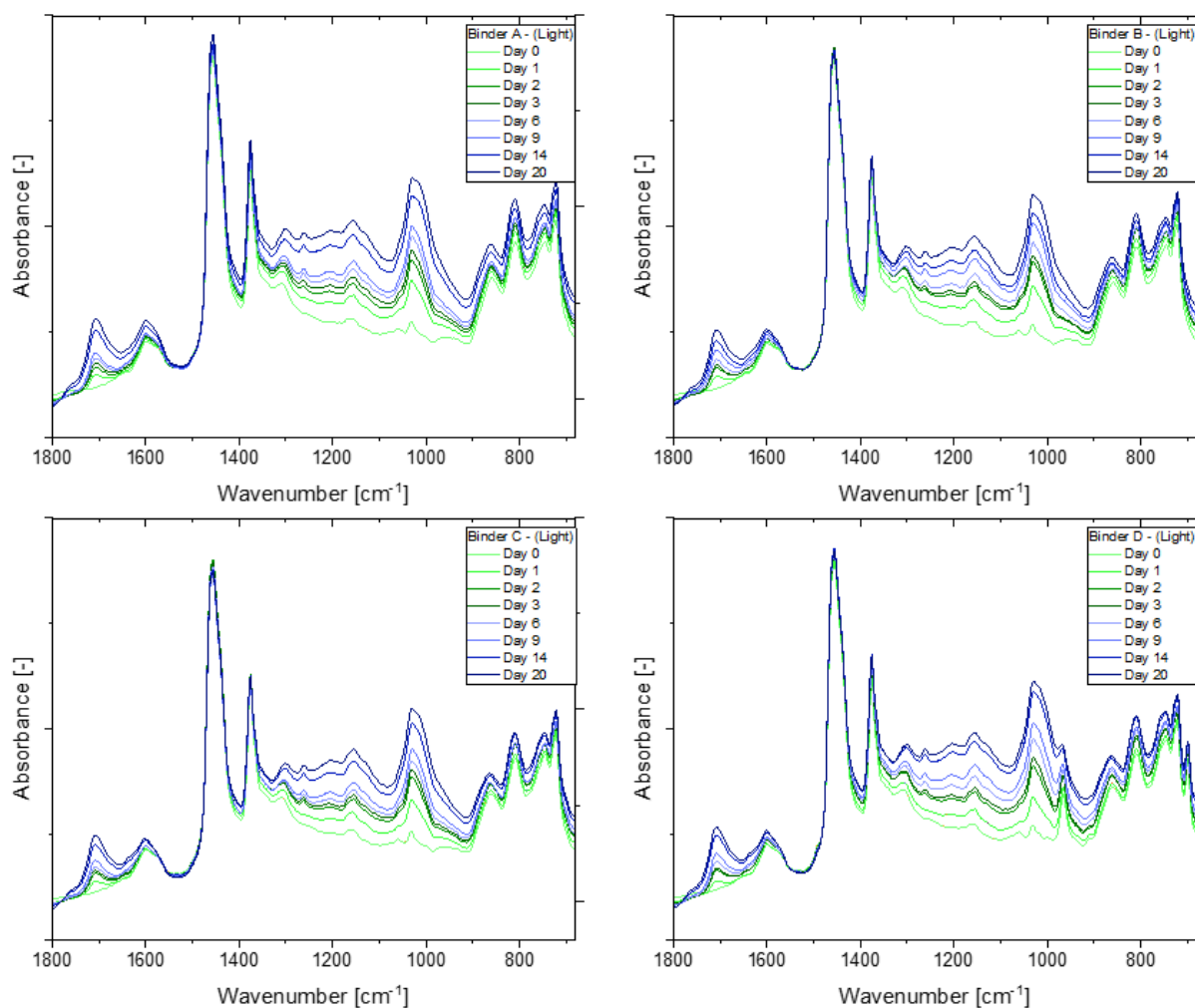
Figure 44: FTIR spectra of unaged binder A – D stored in the light for 0, 1, 2, 3, 6, 9, 14, 20 days.

On the other hand, when the samples are stored in the dark, no significant changes in the spectra of binder A – D can be seen (see Figure 45). The most significant change can be observed in the sulfoxide band (1079 – 984 cm^{-1}) and a slight change at the region of 1260 cm^{-1} and 810 cm^{-1} as the storage time increased. Changes in the region of 1260 cm^{-1} and 810 cm^{-1} can be related to the organic sulphate esters (ROSO$_3^-$) [13].
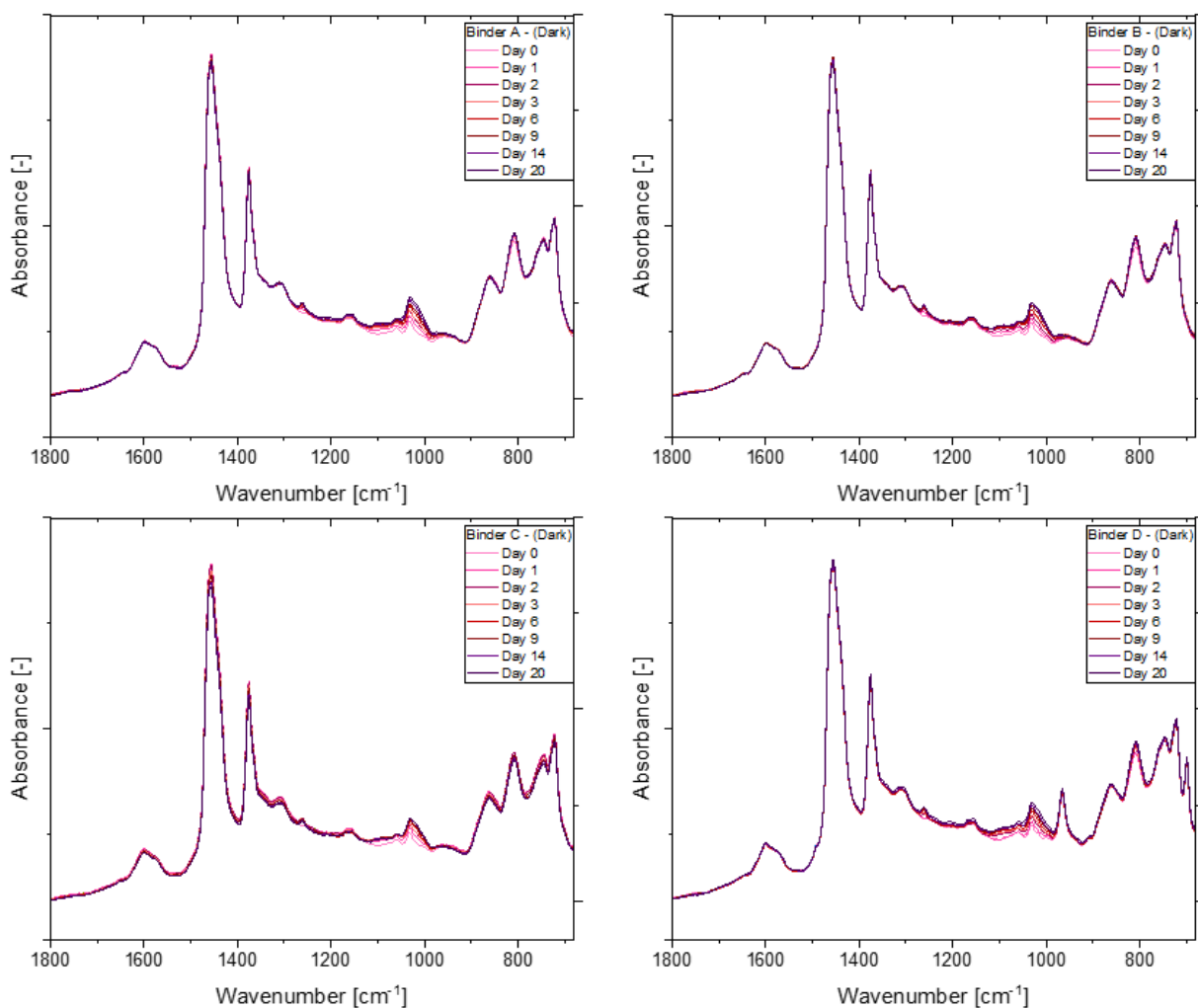
Figure 45: FTIR spectra of unaged binder A – D stored in the dark for 0, 1, 2, 3, 6, 9, 14, 20 days.

Comparing aging indices of binder A stored in the light (see Figure 46 left) and when stored in the dark (see Figure 46 middle) shows that the aging index of the samples stored in the light for only one day exceeds the aging index of the sample stored in the dark for 20 days. On the other hand, comparing aging indices of the RTFOT – aged binder A with the storage time and conditions, it can be seen that only after one day of storing binder A in the light, the RTFOT – aging index of binder A is exceeded, while the binder stored in the dark exceeds the RTFOT – aging index only after the sixth day of storage.

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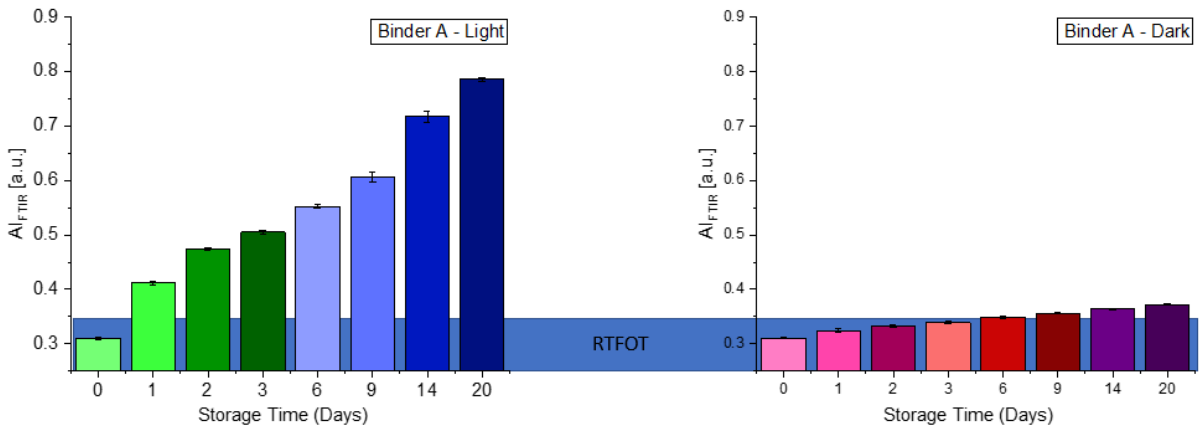
Figure 46: FTIR aging indices of unaged binder A stored in the light (left) and dark (right)

As mentioned before, only the most used binder in Austria (binder B) has been subject of simulation of long-term aging. Therefore, as shown in the Figure 47, a comparison between storage time and conditions to RTFOT+PAV aged binder B is presented. Binder B stored in the light almost reached aging index of long-term aged binder after the first day of storage and exceeds it after the second. Binder B stored in the dark doesn't exceed the long-term aging level, even after stored for 20 days.
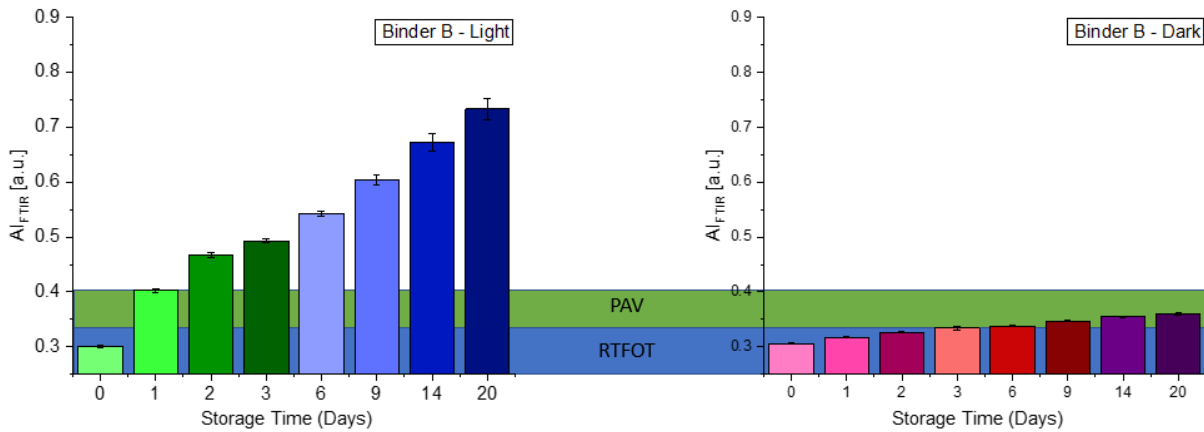
Figure 47: FTIR aging indices of unaged binder B stored in the light (left) and dark (right)

Two following binders (binder C and Binder D) have shown similarities with two previously presented binders (binder A and Binder B). Their aging indices of storage in the light and in the dark, as well the comparison to the RTFOT aged respective binders, can be seen in Figure 48 and Figure 49.

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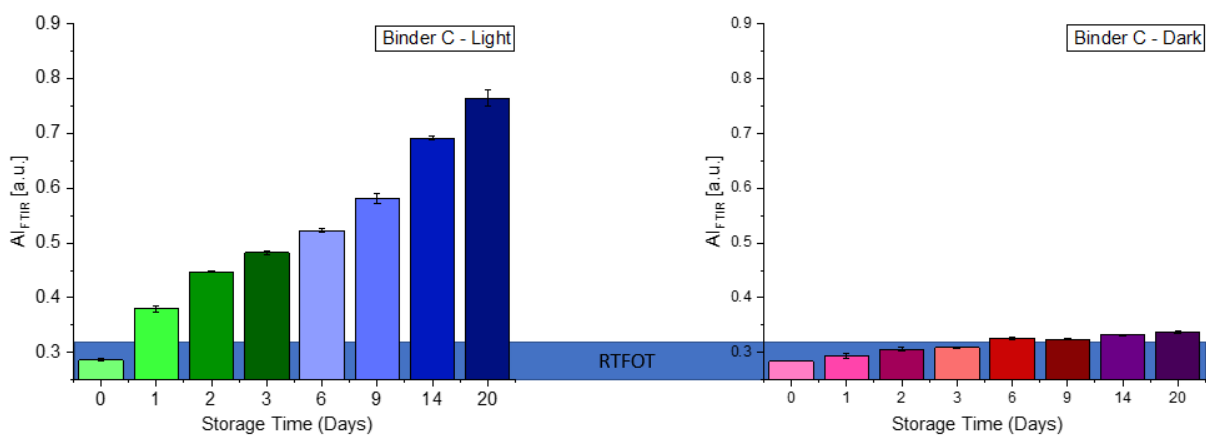
Figure 48: FTIR aging indices of unaged binder C stored in the light (left) and dark (right)
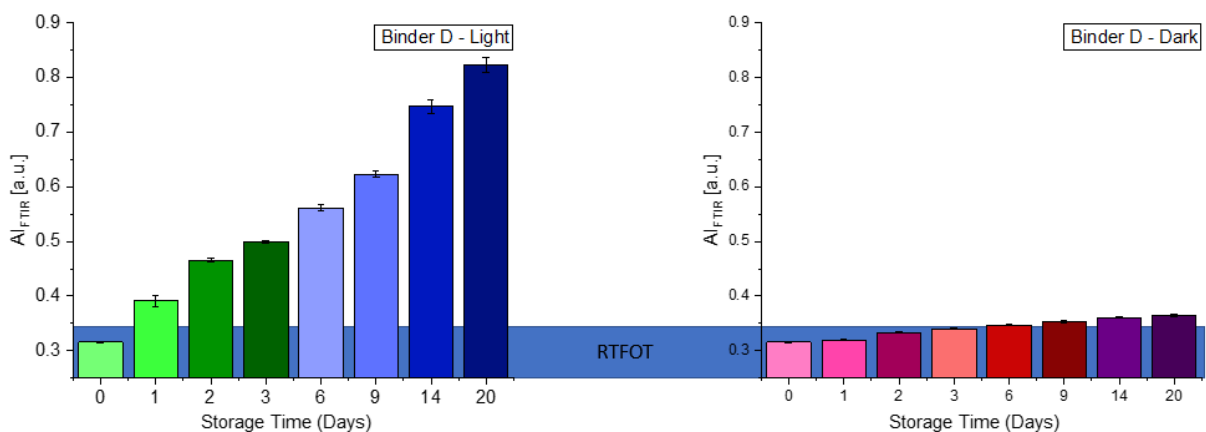
Figure 49: FTIR aging indices of unaged binder D stored in the light (left) and dark (right)

Aging indices and the difference between the shortest and longest storage time of binder A – D stored in the light and in the dark are shown in Table 14.

Table 14: FTIR aging indices of unaged Binder A – D stored in the light and dark after 1, 2, 3, 6, 9, 14 and 20 days

Binder	AI_{FTIR} Day 0	AI_{FTIR} Day 1	AI_{FTIR} Day 2	AI_{FTIR} Day 3	AI_{FTIR} Day 6	AI_{FTIR} Day 9	AI_{FTIR} Day 14	AI_{FTIR} Day 20	ΔAI_{FTIR} (0-20 d)
A – Light	0.310	0.411	0.474	0.505	0.552	0.606	0.717	0.785	0.476
A – Dark	0.310	0.324	0.333	0.339	0.349	0.356	0.364	0.372	0.062
B – Light	0.301	0.403	0.467	0.493	0.542	0.604	0.672	0.733	0.431
B – Dark	0.305	0.318	0.327	0.334	0.338	0.347	0.355	0.360	0.054
C – Light	0.286	0.380	0.447	0.482	0.522	0.582	0.691	0.765	0.476
C – Dark	0.284	0.294	0.306	0.309	0.326	0.324	0.332	0.337	0.053
D – Light	0.316	0.391	0.466	0.499	0.561	0.622	0.747	0.823	0.507
D – Dark	0.316	0.319	0.333	0.340	0.347	0.353	0.360	0.365	0.049

Δ AI$_{FTIR}$ (0-20 d) for binder A stored in the light is (0.476), binder B (0.431), binder C (0.476) and binder D (0.507). Therefore, it can be concluded that all binders stored in the light have almost the same trend of oxidation, except binder D, which has oxidized a little bit more than three others. While Δ AI$_{FTIR}$ (0-20 d) of binder A stored in the dark, is much lower (0.062), binder B (0.054), binder C (0.053) and binder D (0.049). Samples stored in the dark have shown more similarities in the oxidation rate than the samples stored in the light. Oxidation at the surface of samples stored in the dark is caused only by sulfoxides (see Figure 45), since the carbonyls require higher energy to be formed. Hence, the part of the increase in the aging index is due to the increase in sulfoxides.

Figure 50 shows spectra of fingerprint area of binder A – D exposed to visible light for up to 48h. Similar like the previous study, an increase in carbonyls, sulfoxides and overall the fingerprint area can be observed, even after storing the sample for only one hour in the light.
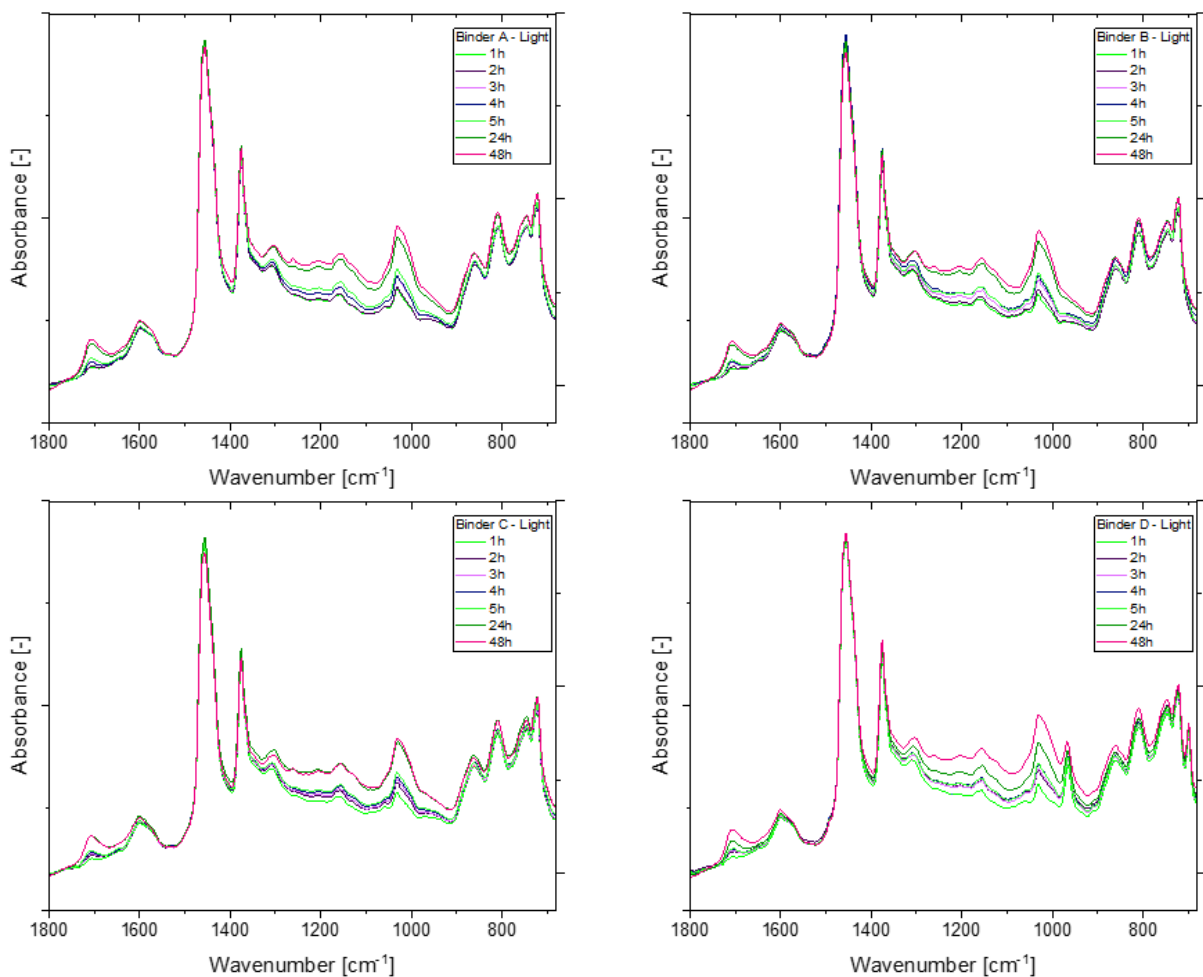
Figure 50: FTIR spectra of unaged binder A – D stored in the light for 0, 1, 2, 3, 4, 5, 24, 48 hours.

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It is important to mention here that when comparing the difference between the shortest and longest storage time (Δ AI$_{FTIR}$ (0-48 h)) in the hours storage study (see Table 15), binder A has shown more similarities with binder B where Δ AI$_{FTIR}$ (0-48 h) is almost indent for these two binders (0.277 and 0.276 respectively). On the other hand, Δ AI$_{FTIR}$ (0-48 h) for the softest binder (binder C) is (0.243), which is almost indent with Δ AI$_{FTIR}$ (0-48 h) of PmB (binder D) (0.245).

Table 15: FTIR aging indices of unaged Binder A – D stored in the light and dark after 1, 2, 3, 4, 5, 24 and 48 hours

Binder	AI$_{FTIR}$ 0 h	AI$_{FTIR}$ 1 h	AI$_{FTIR}$ 2 h	AI$_{FTIR}$ 3 h	AI$_{FTIR}$ 4 h	AI$_{FTIR}$ 5 h	AI$_{FTIR}$ 24 h	AI$_{FTIR}$ 48 h	Δ AI$_{FTIR}$ (0-48 h)
A – Light	0.310	0.361	0.370	0.404	0.402	0.419	0.534	0.587	0.277
B – Light	0.301	0.348	0.375	0.391	0.399	0.412	0.528	0.578	0.276
C – Light	0.286	0.324	0.346	0.360	0.374	0.387	0.504	0.529	0.243
D – Light	0.314	0.351	0.381	0.393	0.403	0.410	0.486	0.559	0.245

As mentioned before these two studies were conducted three months apart from each other. Differences between storing study of the samples in February and May can be seen in Figure 51 ,Figure 52, Figure 53 and Figure 54, where the samples stored for 5 hours in May has exceeded the aging index of the samples stored for one day in February. The RTFOT – aging level of binder A – D was exceeded within one hour of storage in the light. The RTFOT+PAV aging level of binder B was almost reached after storing the sample for four hours and exceeded after 5 hours of storage (see Figure 52).
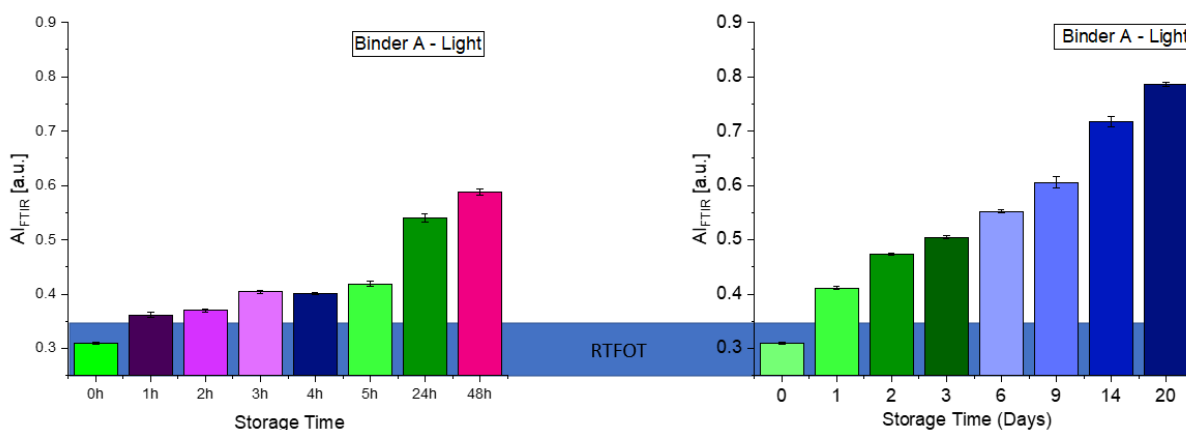
Figure 51: FTIR aging indices of unaged binder A stored in the light for up to 48 hours (left) and stored in the light for up to 20 days (right)

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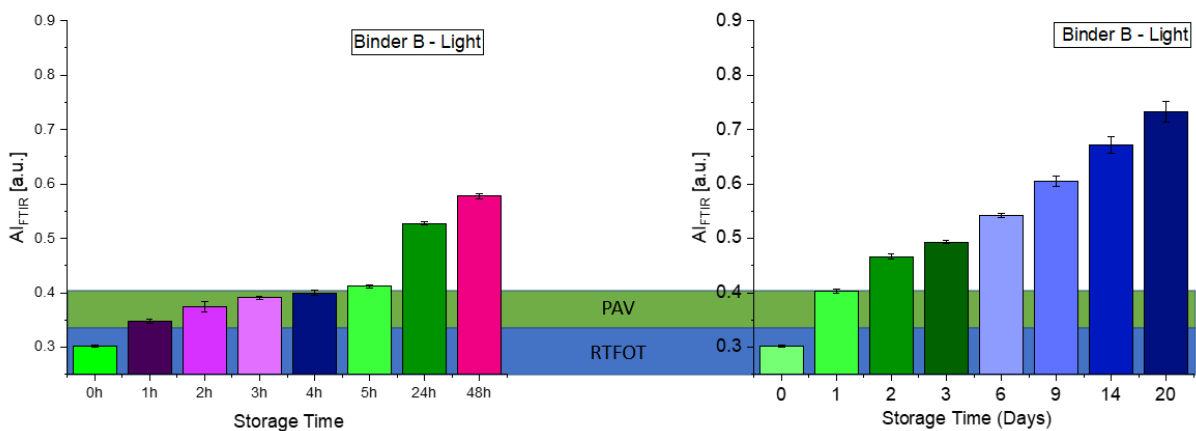
Figure 52: FTIR aging indices of unaged binder B stored in the light for up to 48 hours (left) and stored in the light for up to 20 days (right)
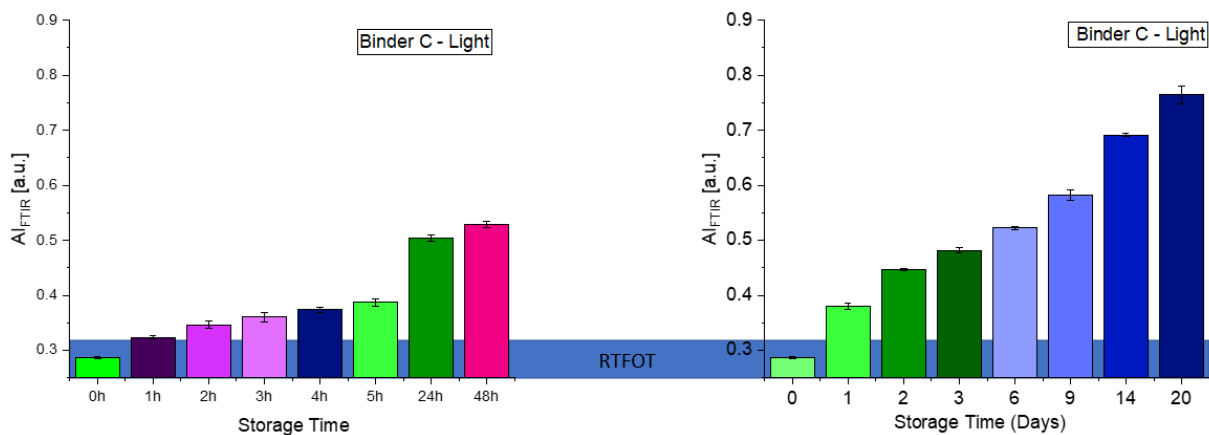
Figure 53: FTIR aging indices of unaged binder C stored in the light for up to 48 hours (left) and stored in the light for up to 20 days (right)
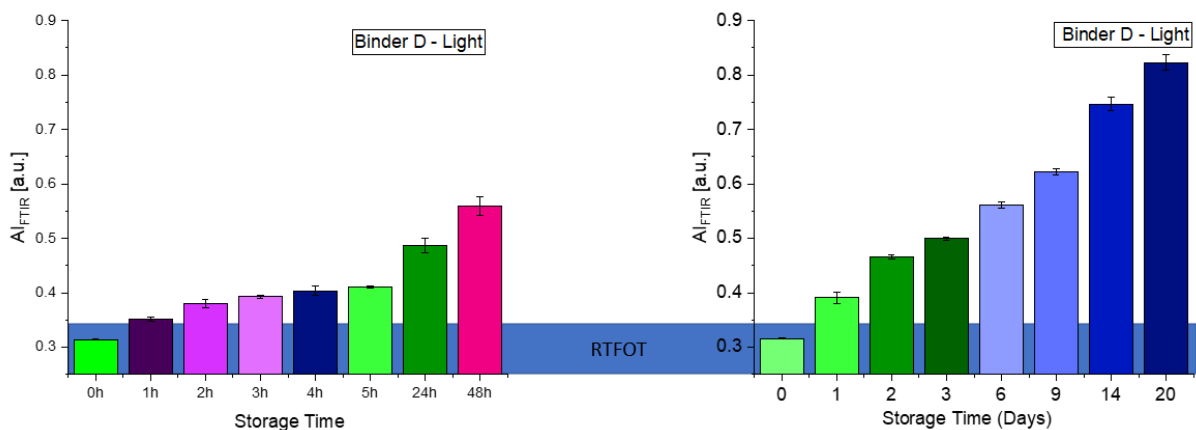
Figure 54: FTIR aging indices of unaged binder D stored in the light for up to 48 hours (left) and stored in the light for up to 20 days (right)

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It also interesting to mention here that when comparing aging indices on the surface of samples stored for 24 and 48 hours in the hours storage study, which corresponds to samples stored for one and two days in days storage study, that samples form hours storage study have clearly oxidized more on their surface that samples from days storage study. This can be explained by the duration of the sunshine. Data from local center of meteorology and geodynamics shows that there were 108 hours of sunshine during February 2021, which is considerably lower than sunshine in May 2021 (182 hours)[1]. This answers the question why samples from May have oxidized more than samples in February, meaning that the energy form light of sunshine in combination with oxygen can cause a significant oxidation on the samples surface.

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[1]

Data for average daily sunshine duration was obtained from the local Center for Metrology and Geodynamics from the following source: https://www.wien.gv.at/statistik/lebensraum/tabellen/luftsonne.html

6 Summary and Conclusion

In this thesis various sample preparation parameters for ATR-FTIR spectroscopy were investigated. Therefore, four binders from the same crude oil source but different specifications classes (A: 50/70, B: 70/100, C: 160:220 and D: PmB) and two different binders within the 70/100 specifications classes (E- and D) from different crude oil source were investigated. All six binders (at unaged state) were used to investigate the influence of heating time (5, 10, 20, 30 mins at 180°) at different heating devices (heating plate and oven). Binder A – D were also investigated at laboratory short term aging state (RTFOT), where binder B also at laboratory long term aging state (RTFOT+PAV).

Furthermore, the binders (A – D) were subject of storage time (1h – 20d) and conditions (light and dark) study to determine the effect on these parameters on the resulting spectra

The goal of this thesis was to investigate the oxidation rate of the above-mentioned binders and give recommendations for conducting FTIR-ATR spectroscopy in regards to achieving good repeatability and reproducibility.

The results show that heating 5 g of bitumen on heating plate for 5 – 10 min and continuous stirring, which ensures proper homogenization, does not induce a significant oxidation, since the recommended threshold value (0.005) is not exceeded. Heating the binder in an open metal can on a ventilated oven is not recommended. The reason for that is because the standard deviation was significantly larger (bad repeatability) and when the binder was heated for 30 mins, it has reached the short-term aging level. Heating the binder in a closed metal can inside a ventilated oven for 5 – 10 mins is also recommended however more difficult to handle in practice.

RTFOT – aged binders (A – D) and RTFOT+PAV – aged binder B did not oxidize much, regardless from heating device, which indicated a lower oxidation susceptibility once the material has aged. Therefore, the samples can be prepared as soon as a good homogenization is reached.

One of the most important factors of the binder aging is storage time and conditions, as the results have shown that storing samples in the light can induce a major oxidation on the samples surface. After just one hour of storing the samples in the light, RTFOT – aging state is reached. Storing samples in the dark leads to a slight formation of sulfoxides as the storing

time increases. Based on the results obtained, it is therefore recommended to store the samples in the dark and measure them within 1 hour after preparation.

The results obtained and the recommendations given are useful for handling such a sensitive material as bitumen when conducting spectroscopic investigations. As the aging indices were evaluated after min max normalization, further data evaluation or more complex approaches can be conducted in the future.

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8 List of Figures

9 List of Tables