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ORIGINAL ARTICLE

FTIR spectral analysis of bituminous binders: reproducibility and impact of ageing temperature

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Abstract This RILEM round robin study with nine participating laboratories investigated bitumen ageing, its effect on chemical properties and its reproducibility. The impact of temperature used for short-term (RTFOT) binder ageing on the combined short- and long-term (PAV) aged samples was investigated; thereby the effect of reduced mixing temperature such as those relevant for warm mix asphalt technologies on long term ageing was examined. Four 70/100 penetration graded bituminous binders from different sources were selected. In addition to the standard RTFOT temperature of 163 °C, two additional temperatures, 143 and 123 °C were used. The Fourier transform infrared spectroscopy (FTIR) analysis was carried out using an integration method which considers the area below the absorbance spectrum around a band maximum using baseline and tangential approaches. A statistical investigation into the reproducibility of FTIR spectra analysis based on the accumulated data was done. To assess the reproducibility, the coefficient of variation (CV) was taken as a benchmark parameter. Carbonyl and sulfoxide indices were calculated using different baseline correction methods and tangential and baseline integration, respectively. It was shown that the tangential method was not influenced by the applied baseline correction. However, in all considered cases, the tangential method led to significantly worse reproducibility (CVs ranging from 20 to 120%) compared

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to the baseline method. The sulfoxide indices calculated by both methods were not affected by the baseline correction method used. Impacts of changes in the short-term ageing temperature on short- or long-term aged samples could not be found whereas differences between different binder sources could be detected. RTFOT temperature and therefore mix production temperature had a stronger impact on the formation of sulfoxide structures than for carbonyl structures. The findings from this study show the most reproducible of all considered methods when more than one laboratory is providing FTIR data.

Keywords FTIR · Bitumen · Asphalt · Oxidation · Ageing · Reproducibility · RTFOT · PAV

1 Introduction

Bituminous binders used extensively in asphalt mixes for construction of pavements are mainly obtained from the refining of crude oil through distillation processes. This material is well-considered as a complex organic matter since it is composed of a large number of hydrocarbons and other elements (mainly O, N, S, and traces of metals). The physical properties of asphalt binders, including its response to applied stress or strain, are highly temperature, time, and loading rate dependent and are thus classified as a viscoelastic substance for mechanistic analysis [1–3]. From a chemical point of view, bituminous binders are sensitive to environmental non-load related actions, mostly oxidative ageing [4, 5]. The oxidative ageing of bitumen occurs in two main stages: in short-term during asphalt mix production while mixing binder and aggregates at elevated temperature (between 140 and 200 °C), transport and compaction; and in long-term when the asphalt mix is in service over time in a pavement structure. Although the mechanism of ageing of bituminous binders is very complex, its consequences on physical and macro-mechanical properties are well-understood. Under sufficient supply of reactive oxygen species in the atmosphere, the oxidative ageing reaction causes the bituminous binder to become stiffer, less temperature susceptible and more brittle, mostly agreed to be upon increasing association among polar components of the binder. While the rheological behavior of bitumen and its change with ageing on the macro-level has been extensively studied in the last decades [6–13] and sophisticated models have been developed to describe the complex behavior of this material [14–20], the chemical composition of bitumen, its changes with ageing, and in-depth analysis of its impact on the mechanical behavior, is still subject to studying [21–28] and intrigue many researchers in chemistry and civil materials engineering fields.

Several methods have been used to analyze the chemistry of bituminous binders including the Corbett chromatography, Gas or Gel Permeation Chromatography and Fourier Transform Infrared Spectroscopy (FTIR). Amongst these techniques, FTIR is a popular method to investigate changes in the chemical composition due to oxidative ageing [29–39]. In general, the objective of absorption spectroscopy, as in FTIR, is to gain information on how much a given sample absorbs light (i.e., infrared radiation) at a certain wavelength range. For mid FTIR, this wavelength usually ranges from 2.5 to 25 µm, which corresponds to wavenumbers from 4000 to 400 cm^{-1}. FTIR makes use of the fact that bonds in molecules absorb infrared light at frequencies that are characteristic for their vibrations, i.e. resonant frequencies. The selection rules for those IR active bands depend inherently on the symmetry of the molecules or molecular groups and are thus related also to the structure of the material. Different groups of molecular bonds can be unambiguously distinguished at different, well-defined wavelengths of an absorbance spectrum by characteristic bands (local maxima in the spectrum) [40]. For bituminous binders, especially those structures associated with oxidative ageing, i.e. uptake of oxygen, have been in the focus of attention in research: (1) The carbonyl functional group has been used to characterize the level of bitumen oxidation and a linear relation between the increase of the log of viscosity and the increase in carbonyl concentration during bitumen ageing procedures has been established [41]. (2) The sulfoxide group is often produced in higher amounts than carbonyl, mainly in bitumen containing high sulfur content. Changes in these chemical groups can then be correlated to changes in

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the rheological properties and allow for a better understanding of chemo-mechanical coupling [42].

Of particular interest is the repeatability and reproducibility of such results. A recent round robin test was performed between seven laboratories using RTFOT aged binders [43]. This study compared Attenuated Total Reflectance (ATR) and transmission spectroscopy and recommends working with transmission spectroscopy since it produces more repeatable results. However, the sample size was very limited (n = 5 for transmission and n = 4 for ATR). Thus, the conclusions of this study are seen as preliminary. Another recent study looked into the repeatability of different approaches to analyze ATR FTIR spectra from bituminous binders [44] in various ageing states from unaged to RTFOT and PAV aged. It was found that integration based methods show a repeatability in terms of coefficient of variation (CV) of 3.0–5.5%.

However, an investigation into the reproducibility of FTIR spectral analysis on bituminous binders with a larger sample size is still missing. Information on reproducibility of FTIR analysis and how to optimize it would potentially improve future research in this field, since it would make results produced by different teams comparable. The results presented here are part of the work of RILEM technical committee chemo mechanical characterization of bituminous materials 252 CMB.

1.1 Objectives and methodology

The central goal of this RILEM round robin testing program is to increase the knowledge on bitumen ageing and its effect on mechanical and chemical properties of the material. The impact of a variation of the temperature (123, 143, 163 °C) used for short-term (RTFOT) binder ageing on the behavior of short- and long-term (PAV) aged samples is in the center of attention. The motivation is to examine the effect of reduced mixing temperature such as in warm mix asphalt technologies on long term ageing. In addition, correlations between mechanical and chemical properties are investigated to better understand the impact of ageing on changes in the chemical composition, and how this affects the observed mechanical behavior.

This paper looks into one part of this extensive study, which is the FTIR analysis of binder samples in different ageing states. The objective is to gather more information on the quality of spectral data obtained from laboratories working with different FTIR setups. In addition, different approaches on how to improve the reproducibility of data received from different participants by state-of-the art manipulations of the individual spectra were investigated. The approach that provided best reproducibility for well-defined indices that describe the state of oxidative ageing was further employed to analyze the impact of short-term ageing temperature on the oxidative ageing of short- and long-term aged binder samples.

1.2 Participating laboratories

The following group of nine laboratories from seven countries, representing academia and industry, participated in the round robin tests:

- Braunschweig University of Technology & University of Kassel, Germany
- Empa, Switzerland
- Michigan Technological University, USA
- Kraton Chemical
- Vienna University of Technology, Austria
- Q8, The Netherlands
- IMP, Switzerland
- Nynas, Sweden
- Repsol, Spain

2 Materials and methods

Four 70/100 penetration graded bituminous binders [45] from different crude sources were used in this study and identified as B501, B502, B503 and B504. In addition, suffixes “A”, “B_Temp” and “C_Temp” were used to give information on the state of ageing: unaged, RTFOT [46] and PAV [47] and on the RTFOT ageing temperature (123, 143 and 163 °C) as exemplified below:

- Unaged binder: A (e.g. B501A)
- RTFOT-aged binder: B_Temp (e.g. B501B_163 for sample B501 aged in the RTFOT at 163 °C)
- PAV-aged binder: C_Temp (e.g. B501C_143 for sample B501 aged in the RTFOT at 143 °C and subsequently in the PAV)

Table 1 provides basic characteristics of the four binder samples according to European Standards [48, 49] and US Performance Grade System [50].

Table 1 Characteristics of bitumen samples

Sample	Penetration at 25 °C (1/10 mm)	Softening point (°C)	PG
B501	77	46.2	70-22
B502	77	47.1	64-22
B503	79	47.5	64-22
B504	84	47.3	64-22

Table 2 FTIR test program

B501	A	B_123	B_143	B_163	C_123	C_143	C_163	B502	A	B_123	B_143	B_163	C_123	C_143	C_163
Lab 1	X		X	X		X	X	Lab 1	X		X	X		X	X
Lab 2	X	X		X	X		X	Lab 2	X	X		X	X		X
Lab 3								Lab 3	X	X		X	X		X
Lab 4	X	X	X		X	X		Lab 4							
Lab 5	X	X		X	X		X	Lab 5							
Lab 6	X			X			X	Lab 6	X			X			X
Lab 7	X	X	X	X	X	X	X	Lab 7	X	X	X		X	X	
Lab 8	X	X	X	X	X	X	X	Lab 8	X	X		X	X	X	X
Lab 9	X	X		X	X		X	Lab 9	X	X		X	X		X
B503	A	B_123	B_143	B_163	C_123	C_143	C_163	B504	A	B_123	B_143	B_163	C_123	C_143	C_163
Lab 1	X		X	X		X	X	Lab 1	X		X	X		X	X
Lab 2	X	X		X	X		X	Lab 2	X	X		X	X		X
Lab 3								Lab 3	X	X		X	X		X
Lab 4								Lab 4	X	X	X		X	X	
Lab 5								Lab 5	X	X		X	X		X
Lab 6	X			X			X	Lab 6	X			X			X
Lab 7	X	X	X		X	X		Lab 7	X	X	X		X	X	
Lab 8	X	X	X	X	X	X		Lab 8	X	X	X	X	X	X	X
Lab 9	X	X		X	X		X	Lab 9	X	X		X	X		X

The values reported in the table were obtained from Laboratory 8.

Table 2 shows an overview of the test program run using the FTIR. The table allocates which laboratory carried out FTIR on which samples for all four binders. In addition, the last row in each table shows how many spectra are available for which sample.

2.1 Laboratory ageing

The entire set of binders was short- and long-term aged. Short-term ageing was performed according to the RTFOT method [46] with a duration of 75 min. In addition to the standard RTFOT temperature of 163 °C, two additional temperatures, 143 and 123 °C, were used to evaluate the effect of temperature on the ageing process. The choice for the reduced temperatures was based on warm mix asphalt technologies. Long-term ageing was conducted using the PAV device [47]. It was carried out after RTFOT at a temperature of 100 °C and an air pressure of 2.1 MPa for 20 h.

Each participant received a batch of unaged bitumen samples and carried out RTFOT and PAV ageing in their own laboratories.

2.2 Sample handling

Detailed instructions on how exactly to handle the different ageing and work steps were delivered with the samples, so that all laboratories treated the samples the same way, especially in terms of thermal history. Therefore, influence of different handling of the samples in the participating laboratories could be kept to a minimum. The work instructions are summarized below

The original binder sample of 2.5 kg was first heated to 160 °C and divided into two equal portions, since each participant was assigned a work program that contained two RTFOT ageing temperatures. The samples were cooled down to room temperature subsequently. Before RTFOT ageing, the binder was reheated to 160 °C for 60 min, so that the initial conditions for the different RTFOT ageing temperatures were the same for all tests. From the liquid binder, different portions were poured into appropriate sample containers to perform mechanical testing (penetration, softening point and dynamic shear rheometer [DSR]) of the virgin binder. Additionally, 10 g were separated into a metal can for FTIR measurements of the virgin binder characteristics. Three RTFOT runs were needed at each temperature to condition sufficient binder to perform all the subsequent tests on aged samples. After the RTFOT ageing step was completed, the binder was again collected in a metal can, homogenized, and cooled down to room temperature. The sample was then reheated to 160 °C for 60 min and binder for the different tests was poured, including for FTIR. 250 g of the RTFOT aged binder went into 5 PAV pans and were PAV aged according to EN 14769 [47]. After the PAV ageing step the pan holders were then put into the oven for 30 min at 170 °C to degas the binder. Then, all pans were poured into one metal can and stirred to homogenize the sample. The PAV aged sample was then poured into the appropriate containers for testing including FTIR.

2.3 FTIR analysis

While a common sample preparation method was defined for all laboratories, each performed the IR spectrometry using their own standard protocol. A survey between the laboratories has shown that all but one used reflectance mode (ATR) and that almost all used different devices and software for data collection from FTIR. Laboratory 6 used transmission mode for IR analysis. Five laboratories used diamond crystal and three laboratories used zinc selenide crystal. In addition, it was common practice to have some pre-processing or calibration before running the analysis.

In terms of test conditions, there was only little variation between the different laboratories. The analysis itself is carried out at room temperature as reported between 18 and 25 °C. The test duration is less than 5 min, most likely within a minute between the time the sample is placed on the crystal and measurement done. The number of scan was 32 for three laboratories, 64 for four laboratories and 24 scans for one laboratory. The resolution was 4 cm^{-1} between 4000 and 400 cm^{-1} wave length for all participating laboratories.

All raw spectra data were submitted by the participating laboratories in a common format. The spectra were merged together and analyzed by one user applying the same analysis methods on all spectra. In this way, any impact of variation of the analysis methods on results could be prevented. The spectra were investigated to obtain information on changes in the chemical composition by oxidative ageing. Therefore, changes in the carbonyl (C=O) and sulfoxide (S=O) area were taken into consideration. The carbonyl area is commonly defined as the band around the 1680 cm^{-1} peak, whereas the sulfoxide area is the band around 1030 cm^{-1}. The aliphatic group (symmetric and asymmetric bending vibrations around 1460 and 1376 cm^{-1}, respectively) is commonly used as a reference group, since it is anticipated that these structures are stable and not affected by applied ageing procedures [51]. The use of a reference group is based on the idea to remove any variation in the absorbance spectra due to a variation of the IR beam penetration between samples, which would bias further interpretation of results.

The spectral analysis was carried out using an integration method which considers the area below the absorbance spectrum around a band maximum. Two state of the art approaches were taken in terms of baseline for integration: (a) the absolute baseline at an absorbance value of 0 and (b) a tangential approach where a relative base line is chosen for each band in a way that the relative base line approaches the spectrum in a tangential way. An FTIR example spectrum indicating all considered structural groups and showing examples of base and tangential integration analysis is presented in Fig. 1.

The integrals from absolute and tangential baseline are defined as follows:

$$I_{i,\text{base}} = \int_{w_{l,i}}^{w_{u,i}} a(w)\,\mathrm{d}w \quad (1)$$

$$I_{i,\tan} = \int_{w_{l,i}}^{w_{u,i}} a(w)\,\mathrm{d}w - \frac{a(w_{u,i}) + a(w_{l,i})}{2} \cdot (w_{u,i} - w_{l,i}) \quad (2)$$

with $a(w)$ absorbance value at wavenumber w, $w_{u,i}$ upper wavenumber limit for structural group i, $w_{l,i}$ lower wavenumber limit for structural group i, $I_{i,\text{base}}$ integrated area from absolute base line for structural group i, $I_{i,\tan}$ integrated area from tangential base line for structural group i.

The lower and upper wave numbers for the structural groups were defined as follows:

- Carbonyl 1660–1753 cm^{-1}
- Sulfoxide 970–1070 cm^{-1}
- Reference (aliphatic) 1350–1525 cm^{-1}

It is to be noted that these upper and lower wave numbers are not absolute and they occur around the peaks mentioned earlier and are material dependent.

From the integrals defined in Eqs. (1) and (2), the carbonyl and sulfoxide indices that are an indication of oxidation are obtained as shown below:

$$\text{ICO}_{\text{base}} = \frac{I_{\text{CO, base}}}{I_{\text{ref, base}}} \quad \text{ISO}_{\text{base}} = \frac{I_{\text{SO, base}}}{I_{\text{ref, base}}} \quad (3)$$

$$\text{ICO}_{\tan} = \frac{I_{\text{CO, tan}}}{I_{\text{ref, tan}}} \quad \text{ISO}_{\tan} = \frac{I_{\text{SO, tan}}}{I_{\text{ref, tan}}} \quad (4)$$

3 Results and discussion

Figure 2 shows FTIR spectra from all unaged binder samples obtained by Laboratory 9 in order to analyze any qualitative differences in the virgin binders. The spectra are stacked starting with B501A on the bottom to B504A on top to make them better distinguishable. While binders B501 to B503 do not show visible differences especially in the relevant bands for oxidation, B504 is different from the other three samples at various positions in the spectrum: in the low wavenumber area below 800 cm^{-1} which is characteristic for aromatic structures, as well as in the sulfoxide area with a lower absorbance and in the carbonyl area with stronger absorbance.

To show the impact of RTFOT and RTFOT + PAV ageing in terms of qualitative changes in FTIR spectra, Fig. 3 contains two diagrams with samples B501 and B504. The reason for choosing these two samples is that B501, B502 and B503 exhibit similar

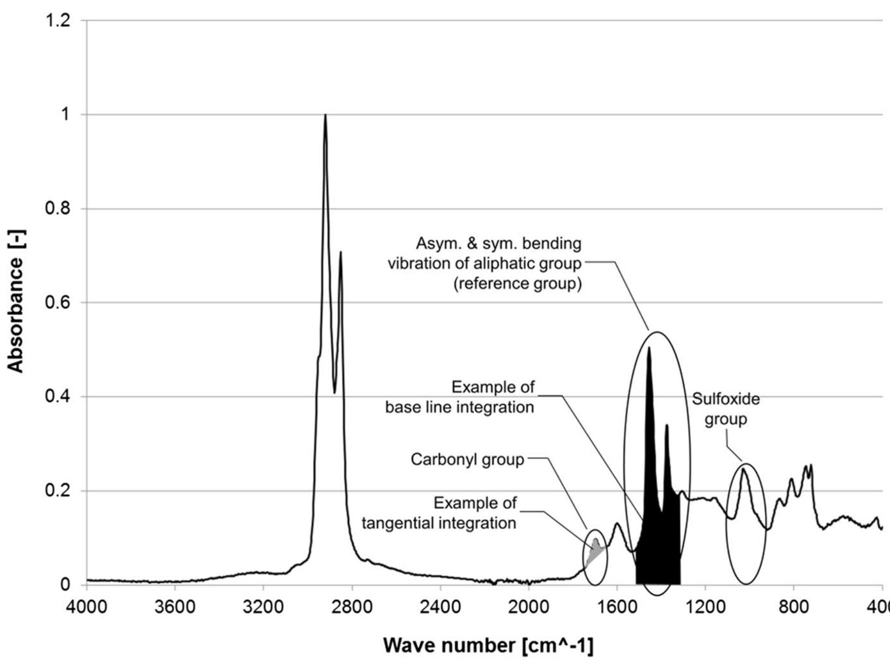

Fig. 1 Example of FTIR absorbance spectrum for an RTFOT + PAV aged binder sample

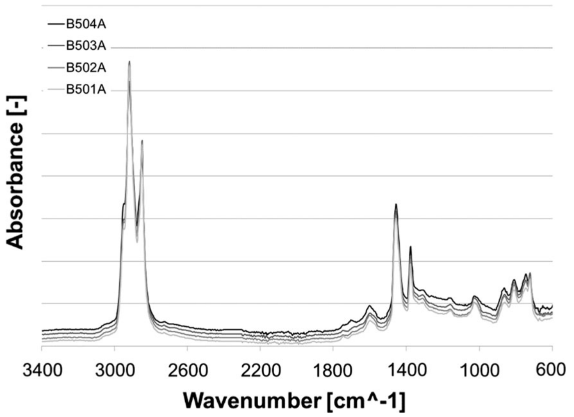

Fig. 2 FTIR spectra of all unaged binder samples from Laboratory 9

spectra, whereas B504 shows some noteworthy differences. Each diagram shows stacked spectra from the unaged sample (light grey), as well as from the RTFOT aged sample at 163 °C (dark grey) and from the RTFOT + PAV aged sample (black). The spectra from Laboratory 9 were zoomed into show only the relevant wavenumber range from 900 to 1800 cm^{-1}. Vertical markers in the diagrams indicate expected band maxima for carbonyl and sulfoxide bands. B504 shows a distinct absorbance in the carbonyl area even in the unaged state. Since the distinct carbonyl area in B504A occurs in spectra from all 9 laboratories, an error, e.g. due to excessive heating prior to FTIR analysis by Laboratory 9 is highly unlikely. The carbonyl group includes a wide range of species, amongst others ester of acid which may be already inherent from the original binder. Thus, the carbonyl peak in the unaged state of B504A is most probably linked to the nature of the bitumen itself either from the origin of the crude oil or the refining process [52, 53].

RTFOT ageing at 163 °C does not lead to a visible increase in the carbonyl area, only after PAV ageing, a distinct band for carbonyl structures can be detected. Interestingly enough, the band maximum of the carbonyl area is slightly shifted for the B504 sample. This is already an important result that the carbonyl peak is not an absolute indicator of oxidation but its increase is a relative indicator of oxidation.

As for the sulfoxide area, all binder samples show absorbance in this band already in the unaged state. The sulfoxide area tends to decrease upon RTFOT ageing and increase again after PAV ageing.

Binder B504A is a valuable sample for this study, since it is the only one that was tested by all 9 participating laboratories to compare spectra received from all laboratories. In addition, since it was tested in its unaged state, any impact of differences in RTFOT and PAV ageing carried out by the different laboratories can be prevented. Figure 4 (top left) shows the spectra as received from the participants in one diagram. The labeling in the spectra follows the sequence of absorbance spectra.

The principal evolution of the absorbance with wavenumber is quite similar for most of the laboratories, Laboratory 6 being an exception since it used transmission mode for IR spectroscopy. All spectra show similar spectra in the aromatic structures range,

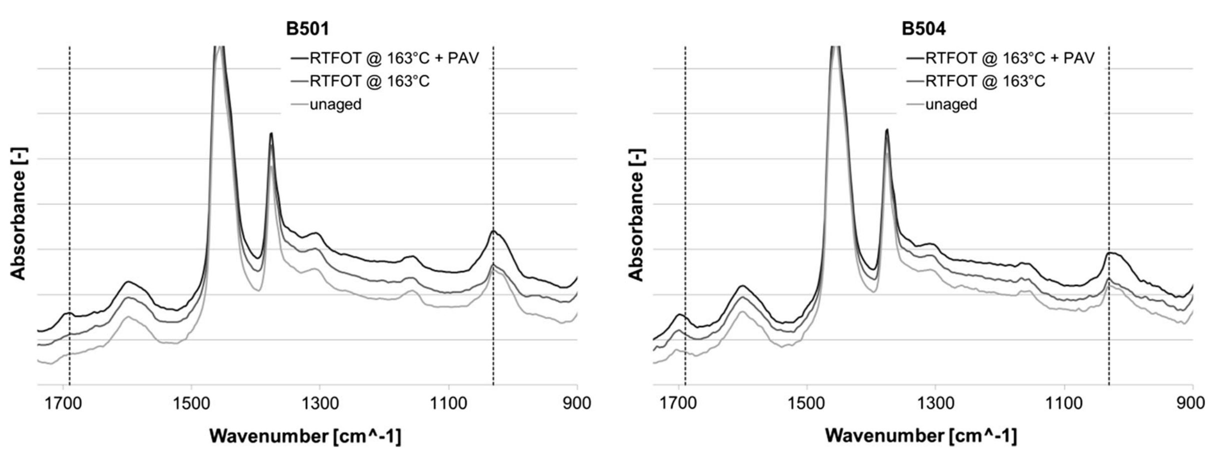

Fig. 3 FTIR spectra of B501 and B504 unaged, RTFOT (163 °C) aged and RTFOT (163 °C) + PAV aged binder samples from Laboratory 9

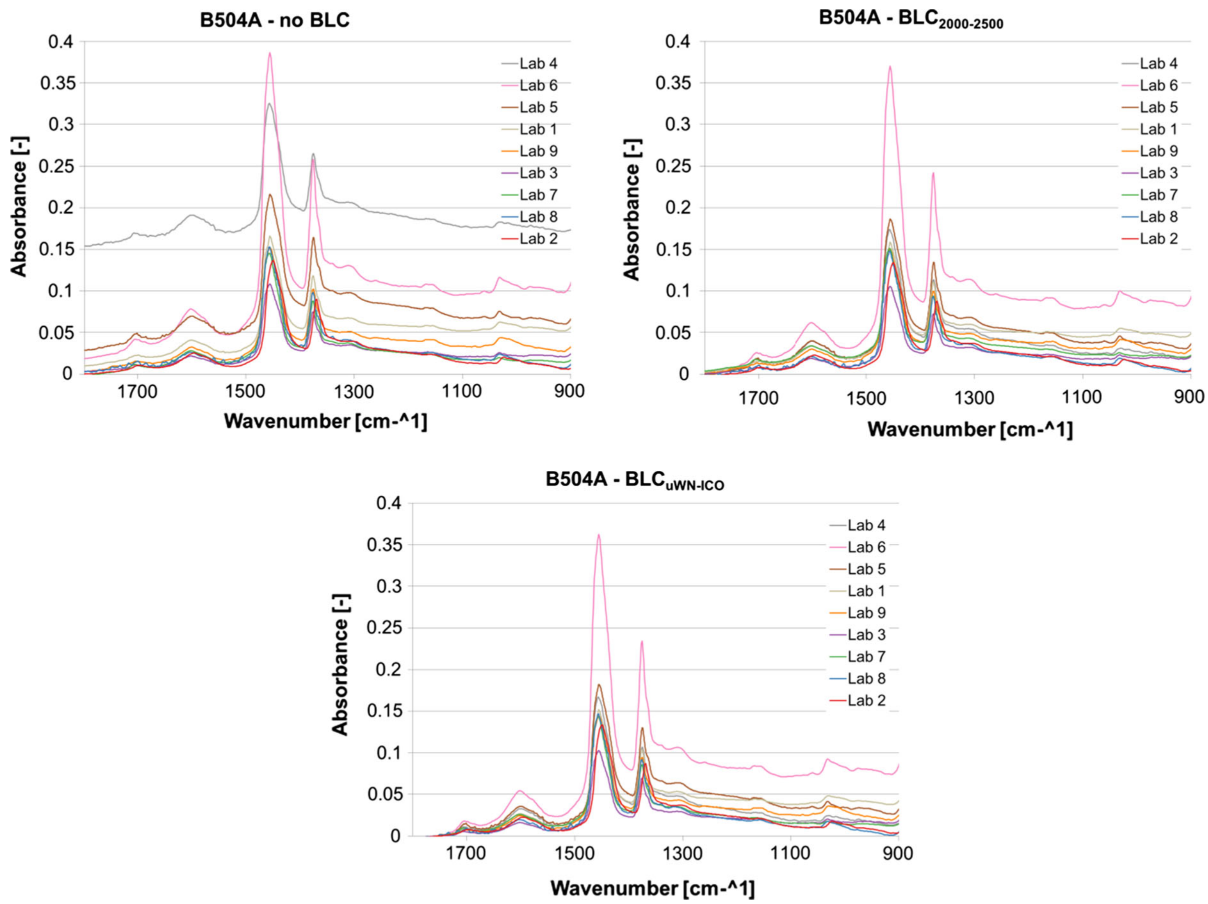

Fig. 4 FTIR spectra of B504A from all participating laboratories, no BLC (top left), $BLC_{2000–2500}$ (top right), $BLC_{uWN\text{-}ICO}$ (bottom)

as well as sulfoxide and carbonyl structures. Also, the aliphatic absorbance band is similar for all laboratories. However, the laboratories differ significantly in terms of their baseline absorbance in the wavenumber range between 2000 and 2500 cm^{-1}. The data in the top left diagram in Fig. 4 shows that a baseline correction may be necessary to bring spectra from different laboratories closer together and therefore enhance comparability of results derived from the spectra.

3.1 Improving reproducibility

Reproducibility referring to comparability of results from different laboratories and repeatability referring results from the same laboratory are important considerations for any experimental method. Assessing the reproducibility of the FTIR method for bitumen is a key result of this round robin test. Although the number of participating laboratories (9) was relatively small for a round robin test, a statistical investigation into the reproducibility of FTIR spectra analysis based on the accumulated data is valuable.

To assess the reproducibility, the coefficient of variation (CV) was taken as a benchmark parameter. Carbonyl and sulfoxide indices were calculated using Eqs. (1)–(4) for each spectrum from each laboratory. Mean values (MV) and standard deviations (SD) for each index and the CV were calculated as the SD relative to the MV in %. The lower the CV, i.e. the lower the scattering of results among the laboratories, the higher is the reproducibility of an index.

Since it was seen from a first visual inspection of the gathered spectra (see e.g. top left diagram in Fig. 4) that they vary strongly in absorbance baseline, three different approach in terms of baseline correction (BLC) were compared: (a) no baseline correction (use spectra as obtained), (b) baseline correction between wavenumber 2000 and 2500 cm^{-1} and (c) baseline correction at the upper wavenumber limit for the carbonyl area (1753 cm^{-1}). The base line corrections (b) and (c) are carried out according to the following equations:

$$BLC_{2000-2500}: \int_{2000}^{2500} (a(w) - c_1)\, dw = 0 \quad (5)$$

$$BLC_{uWN-ICO}: \; a(w_{u,CO}) - c_2 = 0 \mid w_{u,CO} = 1753 \quad (6)$$

with $a(w)$ absorbance value at wavenumber w, c_1 constant for $BLC_{2000–2500}$, $w_{u,CO}$ upper wavenumber limit for carbonyl band, c_2 constant for $BLC_{uWN\text{-}ICO}$.

Equations (5) and (6) are solved, so that c_1 and c_2 are derived for spectra from each laboratory and these constants are subsequently used to shift spectra and realize the baseline correction. Figure 4 shows B504A spectra from all laboratories with no BLC, $BLC_{2000\text{-}2500}$ and $BLC_{uWN\text{-}ICO}$ in the relevant wavenumber range from 900 to 1800 cm^{-1}.

With the three methods at hand, one without baseline correction and two with different baseline correction approaches the carbonyl and sulfoxide indices were calculated for all spectra obtained by the different laboratories for all cases. MV, SD and CV were derived from the calculated indices and CV was used to assess reproducibility.

Table 3 contains the CVs for ICO_{base}, ICO_{tan}, ISO_{base} and ISO_{tan}, respectively. For this analysis, only those cases were taken into account where the number of spectra from different laboratories (sample size) is equal or larger than 6 to have a large enough sample size for deriving meaningful CVs. Numbers highlighted in bold show the lowest CV (best reproducibility) for the two ICO and the two ISO indices, respectively.

Looking at the reproducibility of ICO_{base}, in case no baseline correction was applied, the CV is above 60% in half of the considered cases and still above 40% for most cases. Using $BLC_{2000–2500}$, the CV can be decreased significantly; it does not exceed 60% in any case. Best reproducibility can be achieved, when $BLC_{uWN\text{-}ICO}$ is applied. CVs are around or below 20% for most cases. In addition, it becomes obvious from the data that higher ICOs (PAV aged state) lead to best reproducibility with CVs below 15% and lower ICOs (unaged state) tend to show worse CVs even above 20% for some cases.

Comparing CVs from ICO_{tan} to ICO_{base}, ICO_{tan} is influenced by the applied baseline correction method to a much lesser degree than ICO_{base}. This is understandable since with tangential integration, the baseline for integration is independent of the spectral baseline. However, in all considered cases, ICO_{tan} led to significantly worse reproducibility (CVs ranging from 20 to 120%) compared to ICO_{base}. Looking at data from ISO_{base} and ISO_{tan}, in the majority of the considered cases both sulfoxide indices were not affected by the baseline correction method. In over half of the considered cases, ICO_{base} led to lower CVs than ICO_{tan}. Thus, the given data support the use of integrated indices from absolute base line (ICO_{base} ISO_{base}) with baseline correction method $BLC_{uWN\text{-}ICO}$ to improve reproducibility and thus comparability of data between different laboratories.

The best case results for CVs for reproducibility (10–20% for ICO_{base}) are fairly higher than CVs reported previously for repeatability (see [44]: 3.0–5.5% for ICO_{base}). It has to be taken into account that the reproducibility in this case is not only affected by FTIR but also by preceding ageing procedures RTFOT and PAV that were applied to all binder samples in the participating laboratory. Although RTFOT and PAV were carried out according to the European Standards and in addition, detailed work instructions set binder handling and ageing conditions even more strictly, a certain amount of scattering in the data will have to be attributed to unavoidable differences in laboratory ageing of the binder samples. Taking the three unaged samples (B501A, B502A and B504A) into account which are not affected by any ageing procedure, the reproducibility of these samples is still poorer (11–28%) than the reported repeatability in [44]. Thus, the poorer reproducibility is only partly affected by the preceding ageing procedures. Another part is due to the use of different devices and different operators, respectively.

3.2 Impact of RTFOT temperature on short- and long-term ageing

Employing the findings about optimal approach for high reproducibility in Sect. 3.1, the oxidation indices (ICO_{base} and ISO_{base}) were calculated from $BLC_{uWN\text{-}ICO}$ corrected spectra for all binder samples from all

Table 3 CVs for ICO_{base}, ICO_{tan}, ISO_{base}, ISO_{tan} for all applied baseline correction methods

	B501A	B501B_ 123	B501B_ 163	B501C_ 123	B501C_ 163	B502A	B502B_ 163	B502C_ 163	B503A	B504A	B504B_ 123	B504B_ 163	B504C_ 123	B504C_ 163
ICO-base														
no BLC	76%	106%	58%	79%	44%	64%	29%	31%	41%	71%	99%	33%	64%	38%
BLC(2000-2500)	47%	46%	40%	28%	29%	48%	25%	19%	56%	26%	35%	18%	25%	15%
BLC(uWN-ICO)	**22%**	**23%**	**19%**	**15%**	**14%**	**28%**	**21%**	**10%**	**30%**	**11%**	**18%**	**10%**	**14%**	**10%**
ICO-tang														
no BLC	92%	38%	163%	35%	39%	45%	101%	20%	110%	30%	44%	18%	23%	21%
BLC(2000-2500)	97%	44%	134%	43%	38%	36%	85%	21%	104%	29%	27%	18%	21%	20%
BLC(uWN-ICO)	91%	43%	119%	48%	40%	33%	81%	22%	90%	32%	27%	19%	22%	21%
ISO-base														
no BLC	**31%**	37%	30%	29%	24%	40%	28%	25%	38%	37%	40%	31%	28%	22%
BLC(2000-2500)	32%	**32%**	25%	**19%**	**20%**	38%	29%	26%	37%	**35%**	**26%**	34%	23%	23%
BLC(uWN-ICO)	33%	33%	28%	21%	22%	40%	29%	26%	38%	39%	28%	35%	26%	24%
ISO-tang														
no BLC	37%	72%	23%	26%	29%	29%	**24%**	**10%**	29%	59%	50%	19%	**18%**	8%
BLC(2000-2500)	41%	78%	23%	30%	29%	29%	25%	11%	29%	63%	52%	20%	21%	7%
BLC(uWN-ICO)	41%	79%	**23%**	30%	29%	**29%**	25%	11%	**29%**	64%	54%	**19%**	22%	**7%**

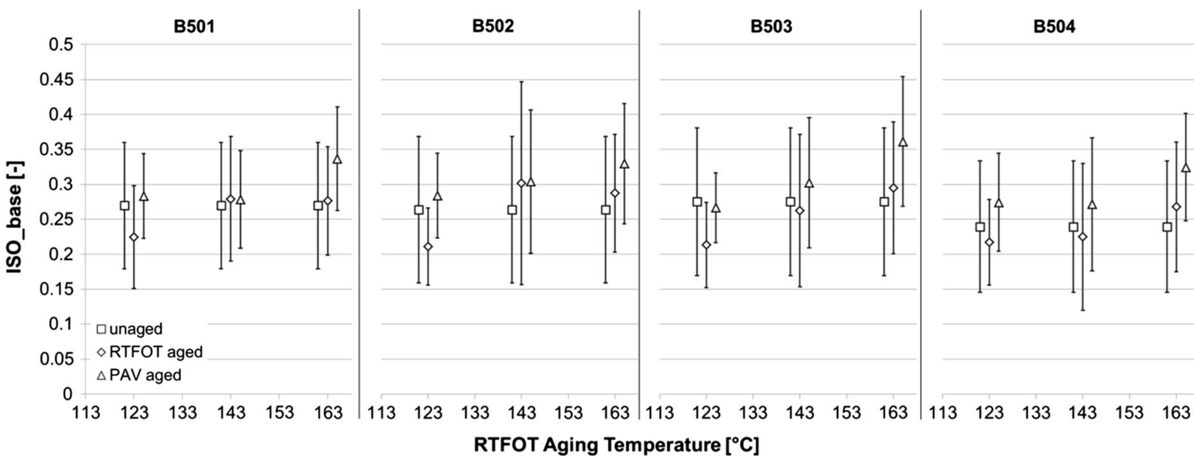

Fig. 5 Evolution of ICO_{base} from $BLC_{uWN\text{-}ICO}$ with RTFOT temperature

participating laboratories. Figure 5 contains ICO_{base} from B501 to B504 and Fig. 6 shows ISO_{base} versus RTFOT ageing temperature. The data in the diagrams are MV, error bars represent SD. In addition, Tables 4 and 5 contain a statistical analysis of results for ICO and ISO, respectively. A statistical *t* test [54] was carried out to investigate significance of differences between indices from different ageing states. Cells highlighted in bold indicate test values below a significance level alpha of 0.05. Thus, highlighted cells show that the respective indices are significantly different.

Combining information from Fig. 5 and Table 4 for the carbonyl index, hardly any changes in ICO can be observed due to RTFOT ageing. There is an increasing trend for B504, but the differences between unaged and RTFOT aged state are not significant. The data shown in the diagrams and tables do not show a significant impact of RTFOT temperature on short-term or long-term aged material regardless of the RTFOT temperature used. PAV aged samples show significantly higher carbonyl indices compared to RTFOT and unaged samples. However, no significant differences between PAV aged samples from RTFOT aged samples at different temperatures could be found.

Comparing B504 to the other three binder samples, B504 shows clearly higher ICOs in all ageing states with ICOs being about 0.01 higher than the other three

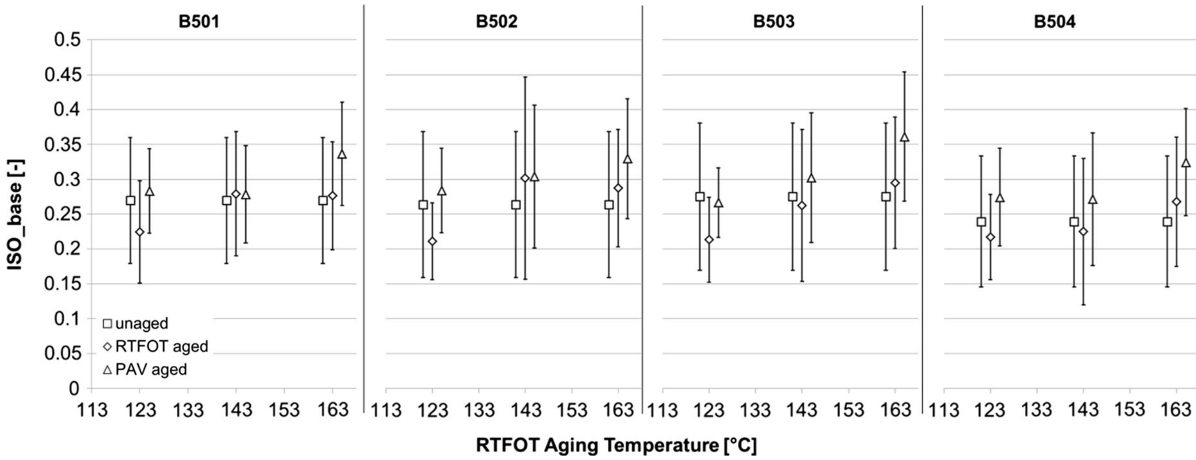

Fig. 6 Evolution of ISO_{base} from $BLC_{uWN\text{-}ICO}$ with RTFOT temperature

binders. This is in line with visual assessment of B504 spectra (Fig. 3) with significant carbonyl bands even in the unaged state as discussed earlier. The results for all four types of binders show that after RTFOT in some cases there is a slight reduction in ICO.

Analysis of changes in the carbonyl bands due to oxidative ageing by FTIR is a discriminant approach when the rather large changes, i.e. from an unaged or short-term aged to a long-term aged state, are considered. Impacts of changes in the short-term ageing temperature on short- or long-term aged samples could not be found by this investigation. Differences between different binder sources can be detected, as shown for the case of B504 compared to the other three binder samples.

Figure 6 and Table 5 show results from the sulfoxide indices vs. RTFOT temperature. Due to the rather small changes with ageing and the larger scattering of results, no significant changes can be found, with one exception, which is from RTFOT aged sample at 123 °C to PAV aged sample after RTFOT at 163 °C. Still, it is interesting that certain trends are observable and are consistent for all four binder samples. In all cases, an RTFOT at 123 °C leads to a decrease of ISO, whereas ISO stays mostly constant at an RTFOT at 143 °C and increases for RTFOT at 163 °C. As for PAV, there is an increase after RTFOT at 123 °C, as well as at 143 and 163 °C. The increase tends to be stronger with increasing RTFOT temperature. Thus, the data show that RTFOT temperature and therefore mix production temperature has a stronger impact on the formation of sulfoxide structures than for carbonyl structures. Also, the long-term aged state after PAV is affected by the short-term ageing temperature.

4 Summary, conclusions and recommendations

This paper presents part of an extensive study on the link between chemical structure and mechanical behavior of bituminous binders carried out by RILEM TC 252 CMB. For the study, a round robin testing program with participation from 9 laboratories, was carried out on four 70/100 pen graded binders from different sources. The samples were short-term aged by RTFOT at three different temperatures (123, 143, 163 °C) and long-term aged by PAV for 20 h at 2.1 MPa and 100 °C. With these samples, impacts of short-term ageing temperature on chemical changes due to short- and long-term ageing of bituminous binders could be investigated. These impacts are of particular interest for the industry, since the market share of warm-mix asphalt mixes (WMA) with decreased production temperatures gains increasing importance, but the impact of lower production temperatures (short-term ageing) on the long-term behavior has not been studied thoroughly yet. Samples were investigated by mechanical tests as well as chemical tests using FTIR analysis. This paper shows an in-depth analysis of the received FTIR spectra from the round robin study. The main purpose of the presented work is to look into methods on how to improve the reproducibility and thus comparability of

Table 4 Results of t-test for ICO_{base} from $BLC_{uWN\text{-}ICO}$ for all binder samples (highlighted are test values below a significance level alpha of 0.05)

ICO_base	B501A	B501B_123	B501B_143	B501B_163	B501C_123	B501C_143
B501B_123	4.6E−01					
B501B_143	2.5E−01	6.6E−01				
B501B_163	1.3E−01	**4.3E−02**	**2.7E−02**			
B501C_123	**7.8E−05**	**8.4E−05**	**2.8E−04**	**1.2E−03**		
B501C_143	**3.2E−04**	**4.1E−04**	**1.7E−03**	**2.4E−03**	6.2E−01	
B501C_163	**7.6E−06**	**1.0E−05**	**4.6E−05**	**1.5E−04**	5.6E−01	9.7E−01
ICO_base	B502A	B502B_123	B502B_143	B502B_163	B502C_123	B502C_143
B502B_123	9.4E−01					
B502B_143	7.0E−02	8.0E−02				
B502B_163	1.2E−01	1.2E−01	3.5E−01			
B502C_123	**6.0E−04**	**1.1E−03**	9.2E−02	**4.8E−03**		
B502C_143	**8.1E−05**	**3.1E−04**	**3.4E−02**	**5.3E−04**	1.6E−01	
B502C_163	**3.3E−06**	**1.1E−05**	**1.7E−02**	**5.3E−05**	4.6E−01	2.3E−01
ICO_base	B503A	B503B_123	B503B_143	B503B_163	B503C_123	B503C_143
B503B_123	5.0E−01					
B503B_143	6.3E−01	2.5E−01				
B503B_163	4.7E−01	8.8E−02	9.1E−01			
B503C_123	**5.5E−03**	**2.6E−03**	**2.2E−02**	**7.6E−03**		
B503C_143	**1.0E−03**	**9.8E−04**	**8.3E−03**	**1.4E−03**	2.2E−01	
B503C_163	**2.5E−03**	**1.6E−03**	**1.2E−02**	**3.6E−03**	4.6E−01	6.3E−01
ICO_base	B504A	B504B_123	B504B_143	B504B_163	B504C_123	B504C_143
B504B_123	1.6E−01					
B504B_143	**3.3E−02**	5.2E−01				
B504B_163	**3.0E−04**	9.6E−02	3.0E−01			
B504C_123	**2.5E−06**	**1.8E−04**	**8.5E−04**	**6.3E−04**		
B504C_143	**8.0E−07**	**7.3E−05**	**6.5E−04**	**1.3E−04**	3.6E−01	
B504C_163	**3.9E−08**	**2.1E−05**	**1.4E−04**	**3.8E−05**	8.5E−01	3.6E−01

FTIR data received from different laboratories, working with different equipment. Thus, the findings from this study may not represent the most sensitive method of analyzing FTIR spectra for bituminous binders, but the most reproducible of all considered methods. After improving the reproducibility, the impact of short-term ageing temperature on oxidative uptake during short- and long-term ageing was investigated. Oxidative uptake is assessed using changes in the carbonyl (C=O) and sulfoxide (S=O) bands.

A first visual inspection of spectra derived from the participants showed that all spectra exhibit similar absorption bands, however the baseline absorbance varied greatly between the laboratories. Thus, to improve the reproducibility of derived carbonyl and sulfoxide indices, two different baseline correction methods were considered. In addition, two approaches for index calculation were used: integration using the absolute baseline and a tangential baseline, respectively. The results of this analysis showed that a baseline correction that sets the absorbance spectra at the upper wavenumber limit of the carbonyl band (1753 cm^{-1}) to zero ($BLC_{uWN\text{-}ICO}$) in conjunction with integration using the absolute baseline leads to lowest coefficients of variations (CV) (best reproducibility) for all considered samples. This approach leads to a decrease of the CV from 60 to 100% (no baseline correction) to around 20%. Tangential integration resulted in worse reproducibility for both, the carbonyl and sulfoxide indices.

Table 5 Results of t-test for ISO_{base} from $BLC_{uWN-ICO}$ for all binder samples (highlighted are test values below a significance level alpha of 0.05)

ISO_base	B501A	B501B_123	B501B_143	B501B_163	B501C_123	B501C_143
B501B_123	3.2E−01					
B501B_143	8.7E−01	3.4E−01				
B501B_163	8.8E−01	2.4E−01	9.6E−01			
B501C_123	7.4E−01	1.6E−01	9.4E−01	8.6E−01		
B501C_143	8.5E−01	2.7E−01	9.9E−01	9.6E−01	9.1E−01	
B501C_163	1.4E−01	**1.9E−02**	3.0E−01	1.6E−01	1.8E−01	2.3E−01
ISO_base	B502A	B502B_123	B502B_143	B502B_163	B502C_123	B502C_143
B502B_123	2.8E−01					
B502B_143	7.4E−01	4.3E−01				
B502B_163	6.6E−01	1.0E−01	9.0E−01			
B502C_123	6.9E−01	8.3E−02	8.7E−01	9.3E−01		
B502C_143	5.9E−01	2.0E−01	9.9E−01	8.2E−01	7.7E−01	
B502C_163	2.4E−01	**2.2E−02**	8.1E−01	4.1E−01	3.3E−01	7.2E−01
ISO_base	B503A	B503B_123	B503B_143	B503B_163	B503C_123	B503C_143
B503B_123	2.7E−01					
B503B_143	8.7E−01	5.1E−01				
B503B_163	7.5E−01	1.6E−01	6.8E−01			
B503C_123	8.7E−01	2.3E−01	9.5E−01	5.8E−01		
B503C_143	7.0E−01	2.1E−01	6.5E−01	9.2E−01	5.7E−01	
B503C_163	2.1E−01	**3.7E−02**	2.6E−01	3.3E−01	1.2E−01	4.4E−01
ISO_base	B504A	B504B_123	B504B_143	B504B_163	B504C_123	B504C_143
B504B_123	5.8E−01					
B504B_143	8.2E−01	9.0E−01				
B504B_163	5.5E−01	2.5E−01	5.1E−01			
B504C_123	4.1E−01	1.3E−01	4.2E−01	8.8E−01		
B504C_143	5.8E−01	3.3E−01	5.4E−01	9.5E−01	9.6E−01	
B504C_163	6.6E−02	**1.4E−02**	1.3E−01	2.4E−01	2.3E−01	3.7E−01

Based on these findings, the second part of the study looked at the impact of short-term ageing temperature on carbonyl and sulfoxide indices using the $BLC_{uWN-ICO}$ and absolute baseline integration. It was found that for the carbonyl index, hardly any changes could be observed due to RTFOT ageing and no significant differences between RTFOT temperatures were detected. However, significant differences were observed after long-term ageing. PAV aged samples showed a higher ICO than unaged and RTFOT aged samples. No significant impact of RTFOT temperature on PAV aged samples could be seen. Changes in the sulfoxide indices were smaller with larger scattering. Certain trends could be observed which were consistent for all four binder samples. For example, in all cases, an RTFOT at 123 °C led to a decrease of ISO relative to the unaged, whereas ISO stayed mostly the same for RTFOT at 143 °C and increased for RTFOT at 163 °C. As for PAV aging, there was an increase of ISO after RTFOT at 123 °C, as well as at 143 °C and 163 °C. The increase is stronger with increasing RTFOT temperature. Thus, the data shows that RTFOT temperature and therefore mix production temperature has a stronger impact on the formation of sulfoxide structures than for carbonyl structures.

Based on the outcome of the study, the following conclusions and recommendations can be given:

To ensure and improve reproducibility of results gathered from different laboratories, a strict sample handling procedure needs to be followed by all groups. This ensures that the thermal history of all samples in different laboratories is comparable.

- FTIR device, software for data collection and type of crystal (diamond or zinc selenide) used for spectroscopy does not show a systematic effect on received raw spectra. Especially the absorbance baseline varied strongly between the different laboratories, but no link between FTIR setup and this effect could be found. All but one laboratory worked with reflective spectroscopy. One laboratory used transmission spectroscopy.
- For inter-laboratory studies, any manipulation of the raw spectra should be carried out using one software and preferably by one user to prevent any impact of these parameters on the obtained indices.
- A baseline correction shifting all spectra to zero at the upper wave number limit of the carbonyl band (1753 cm^{-1}) in combination with a band integration using the absolute baseline improved the reproducibility of the carbonyl index strongly and left the sulfoxide index unaffected. Thus, for inter-laboratory studies, it is recommended to work using this approach to make data from different laboratories comparable. However, this method may not be the most sensitive method in terms of detecting changes due to oxidative ageing or impacts of ageing conditions, like the temperature. An investigation including repeatability and sensitivity of FTIR spectral analysis can be found in [44].
- Regarding impact of short-term ageing temperature on oxidative changes in short- and long-term aged samples, the FTIR approach used for this study could not show statistically significant impact of RTFOT temperature on short- and long-term aged binders. This is true for the carbonyl and sulfoxide indices. Significant differences can be observed between unaged or RTFOT aged samples and PAV aged samples in terms of Carbonyl Index, but not in terms of Sulfoxide Index.
- The short-term ageing temperatures shows certain patterns for all four considered samples in the sulfoxide bands. RTFOT at 123 °C leads to a decrease, whereas ISO stays mostly the same at RTFOT at 143 °C, and increases for RTFOT at 163 °C. As for PAV, there is an increase in the average values after RTFOT regardless of the temperature, but the increase is not statistically significant and is well within the variability of the results. The increase is somewhat stronger with increasing RTFOT temperature.
- The scatter in the results of both FTIR indices is very significant and the results of unaged and RTFOT for all temperatures almost always overlap. This is a concern as it is known that mechanical properties are highly affected by the RTFOT aging temperature. It is also of concern that for the Sulfoxide Index the results show high scatter and similar ranges for all aging conditions including the PAV aging.

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Compliance with ethical standards

Conflict of interest The authors state that no conflicts of interest exist.

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