Identification of structural changes in bitumen due to aging and fatigue

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ABSTRACT

Bitumen is one of the basic constituents, together with aggregates, which is used to prepare asphalt mixtures for pavement applications. This material is temperature susceptible and subject to oxidative ageing. Bitumen is commonly modelled as a colloid with asphaltenes as the dispersed phase and maltenes as the continuous phase. Additional phenomena such as stress and fatigue effects can influence the structure of bitumen and, ultimately, affect pavement performance and durability. In the present research, the effect of ageing and fatigue stresses on the microstructure and on the molecular components of bitumen is investigated. A plain bitumen 50/70 and a polymer modified bitumen 25/55-55 were evaluated in two different ageing conditions: virgin and aged. The influence of fatigue stress was taken into account by performing shear tests with the Dynamic Shear Rheometer. Thin-layer chromatography, infrared spectroscopy and atomic force microscopy (AFM) were then used to evaluate the structural changes in the materials associated to ageing and fatigue. The results of the chromatographic analysis suggest that the structural changes are proportional to the variation in the bitumen fractions (resins, aromatics, saturated hydrocarbons). The infrared spectroscopic analysis was proven to be suitable for detecting structural changes of virgin, aged and fatigued bitumen. This was confirmed by variations in intensity of transmission spectra due to increased or decreased molecular vibrations of functional groups for specific wave numbers. AFM microscopic analysis showed significant changes in the surface bee-structures between virgin and aged bitumen. The selected experimental methods were able to distinguish microstructural and molecular variations due to ageing and fatigue providing evidence that the mechanical response of bitumen is linked to the physical and chemical properties which are critical for achieving durable and consistent asphalt pavement performance.

Keywords: Ageing, Mechanical Properties, Modified Binders, Testing

1. INTRODUCTION

Bitumen represents a fundamental component of mixtures (air voids, bitumen and aggregate) used for asphalt pavements. The properties of this material significantly influence the response and the performance of asphalt mixture ultimately affecting the durability and the service life of the road infrastructure [1,2].

Conventionally, bitumen is characterized through empirical methods, such as Penetration [3] and Ring and Ball [4], or with mechanical tests which make use of more advanced devices such as the Dynamic Shear Rheometer (DSR) [5]. These methods provide overall information on the bulk material properties through specific parameters; for example complex shear modulus and phase angle [5]. However, a consistent and long term performance of asphalt mixture is, on one side, strongly linked to the understanding of bitumen microstructure and ageing [6], and, on the other, to the evolution of the microstructure when subjected to repeated loading.

Bitumen is generally defined as a “virtually involatile, adhesive and waterproofing material derived from crude petroleum (or present in natural asphalt) which is completely or nearly completely soluble in toluene, and very viscous or nearly solid at ambient temperature” [6,7]. Average molecular structures have been proposed for bitumen in the past during the SHRP study [8]. However, bitumen properties can be better investigated by separating the molecules into different chemical families, depending on their size and solubility in polar, aromatic or non-polar solvents [6] assembled into a colloidal structure [6]. Corbett was among the first in separating bitumen in the so called SARA fractions, Saturates, Aromatics, Resins and Asphaltenes, resulting into a bitumen structure made of a chemical continuum with a gradual increase of molar mass, aromatic content and polarity from saturates to asphaltenes [9].

More recent research efforts have addressed the bitumen microstructure with different experimental techniques. Masson et al. [10] used thin-layer chromatography (TLC) with flame ionization detection (ID) for separating bitumen in the different SARA factions. In the same study the effect of chromarod ageing on the reproducibility of the results obtained with this technique was also evaluated. Other authors have used TLC for addressing the impact of polyphosphoric acid [11] and of weathering degradation [12] on bitumen, identifying TLC as a suitable experimental approach.

Fourier Transform Infrared (FTIR) – Attenuated Total Reflectance (ATR) spectroscopy is a robust and accurate non-invasive alternative method that can provide short-time results for identifying the various functional groups present in the material. A number of studies were proposed over the years to investigate the microstructure of bitumen through the FTIR-ATR technique. A comprehensive research on the practical application of this experimental method on bitumen was performed by Nasrazadani et al. [13] indicating that FTIR-ATR is valuable tool for discriminating different polymer modifications. A recent research effort has addressed the effect of ageing on the chemical changes in bitumen; an increase in the absorbance of the carbonyl and sulfoxide IR functional groups was observed [14]. FTIR-ATR was also recently used to evaluate the influence of the physical state of water in the diffusion process within bitumen [15]. Water showed strong absorption in the infrared range indicating that FTIR-ATR technique has the ability to monitor both moisture kinetics as well as any chemical change occurring during the test.

The microstructure of bitumen can be characterized, at surface level, through the Atomic Force Microscope (AFM). This imaging tool provides information on the topography and phase contrast of the sample surface and was found to be particularly useful for multi-phase materials, such as bitumen. In addition AFM is also relatively easy to operate since tests are performed under ambient conditions. This device has recently received significant attention in the research area of asphalt materials. The presence of wax in bitumen and its relation with the glass transition temperature were evaluated by Soenen et al. [16] with AFM. The microstructural properties of bitumen as function of ageing were also addressed in two recent studies [17,18]; the characteristic surface bee-structures were quantified based on AFM technique, showing a decrease of these microstructure shapes for aged material, in one case [17], and an increase in the other [18]. An interesting application of AFM was proposed in two different papers; in these works the blending zone between virgin and aged bitumen was visualized with the objective of improving the understanding of the recycling process of asphalt pavement [19,20].

Although all the methods listed in this introduction section provide significant information on material microstructure, they cannot address all the areas (molecular size, molecular weight, polarity, etc.) within which structural changes occur. Consequently, several methods have to be selected and used to cover the main potential changes in the material microstructure.

2. OBJECTIVE AND RESEARCH APPROACH

In this paper, three experimental techniques are used with the objective of investigating the effect of three different bitumen conditions, virgin, aged and fatigued, on the material microstructure. For this purpose, two types of bitumen where selected and aged, first, according to the Rolling Thin Film Oven Tests (RTFOT) [21] and, then, with the Pressure Ageing Vessel (PAV) procedures [22]. At the same time, DSR fatigue [5] tests were performed on virgin material to obtain fatigue bitumen samples. The changes in microstructural fractions and functional groups were then addressed through thin-layer chromatography with flame ionization detection (TLC-ID) and with FTIR-ATR techniques, respectively. Finally, AFM was used to evaluate the evolution of the surface characteristics of bitumen for the different material conditions.

3. MATERIAL AND DSR TESTING

An unmodified 50/70 bitumen and a polymer modified (styrene-butadiene-styrene - SBS) 25/55-55 bitumen were used in this study. Table 1 provides a summary of the basic characteristics of the virgin material.

Table 1: Bitumen properties

Property	50/70	25/55–55 A
Penetration [1/10 mm]	50	45
Softening Temperature [°C]	51.9	59.7
Shear modulus G^* [kPa] T=60°C	3.7	5.9
Phase angle δ [°] at T=60°C	83.8	71.6

In order to investigate the relationships between chemical constituents and physical properties, the bitumens were long term aged with a combination of RTFOT [21] and PAV methods [22]. In the case of TLC-ID tests only RTFOT specimens were prepared to differentiate the ageing conditions with respect to the other two tests: FTIR-ATR and AFM. In addition, to evaluate the effect of stresses on the bitumen microstructure, DSR [5] fatigue tests were conducted. Therefore, three different bitumen conditions were identified: virgin, aged and fatigued. DSR fatigue tests were performed at T=40°C at a frequency f=10Hz with a strain γ=6% using a 25mm plate-plate geometry. The tests were conducted for t=25200s (~7h) till a significant drop in G^* was observed (Figure 1). The material was then removed from the plates and used for the microstructural characterization.

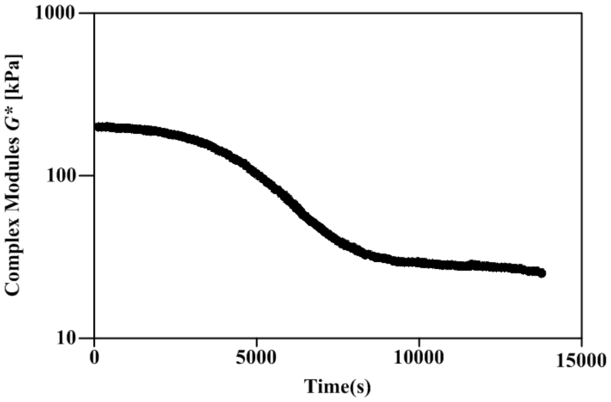


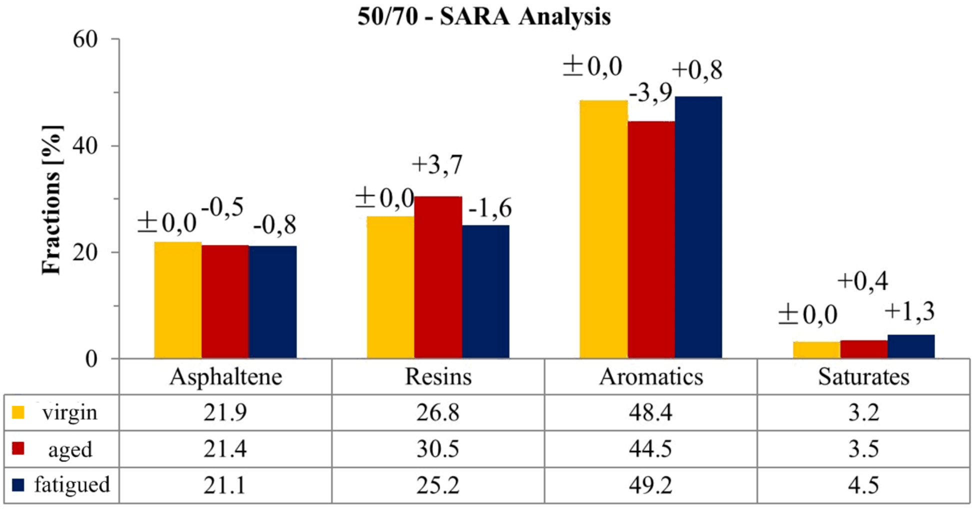
Figure 1: Decay in the shear modulus of the 50/70 bitumen

4. MICROSTRUCTURAL ANALYSIS OF BITUMEN

In this section the structure of bitumen is analysed with three different experimental methods: TLC-ID, FTIR-ATR and AFM. The results are presented and discussed in the next three subsections.

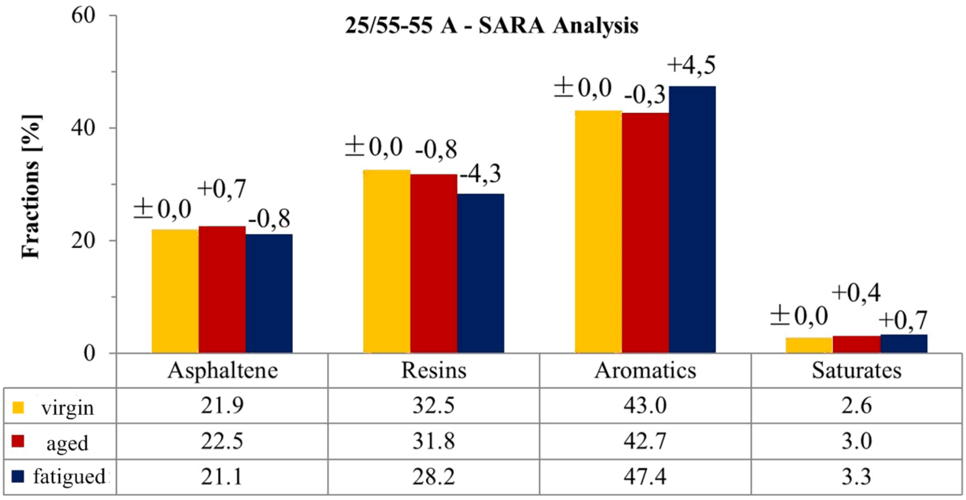
4.1 Chromatographic analysis

The chromatographic analysis and the determination of SARA fractions were performed on both bitumens with an Iatroscan TLC / FID MK device. For each condition (virgin, aged and fatigued), SARA fractions were determined on three replicates and the change over the three conditions was calculated. The significance of the results was verified with a simple t-statistical test [23]. The results for both bitumens are shown in Figures 2 and 3.



	Asphaltene	Resins	Aromatics	Saturates
🟨 virgin	21.9	26.8	48.4	3.2
🟥 aged	21.4	30.5	44.5	3.5
🟦 fatigued	21.1	25.2	49.2	4.5

Figure 2: SARA analysis for bitumen 50/70



	Asphaltene	Resins	Aromatics	Saturates
🟨 virgin	21.9	32.5	43.0	2.6
🟥 aged	22.5	31.8	42.7	3.0
🟦 fatigued	21.1	28.2	47.4	3.3

Figure 3: SARA analysis for bitumen 25/55-55 A

The 50/70 bitumen presents in its virgin state high percentage of aromatics, while saturates are, in turn, proportionately very small (3.2%). Asphaltenes (21.9%) and Resins (26.8%) present similar proportions. With respect to the virgin condition the RTFOT aged bitumen shows significant changes across the different SARA fractions, with increased resins content. Relatively larger variations can be observed for the fatigued bitumen where a decrease in resins and an increase in the aromatics components, together with a proportional increase of saturated hydrocarbons, were found.

Similar proportions of the SARA fractions were found for the modified 25/55-55 A bitumen in virgin state; the largest difference accounts for a higher resins amount and a lower aromatics content in the order of 5%. An increase of asphaltenes by 0.7% can be observed for the aged condition. The saturated hydrocarbons increases of 0.4% while resins decreases of 0.8%. As for the unmodified bitumen larger variation in the SARA fractions is found in the fatigued bitumen for resins (-4.3%) and Aromatics (+4.5%).

4.2 Spectroscopic analysis

Another method to investigate bitumen at the molecular level is given by infrared spectroscopy. Here, transmission spectra are determined as function of the transmittance of a sample in the infrared range. Therefore, changes at the molecular level due to different material conditions can be detected in the transmission and absorption spectra.

In this study infrared spectroscopic analysis was performed using a Fourier transform IR spectrometer Equinox 55 of Bruker Optics with attenuated total reflectance (ATR). For each condition (virgin, aged and fatigued) three replicates per bitumen type (50/70 and 25/55-55 A) were subjected to FTIR-ATR tests. The transmission spectra were obtained as the mean in a wavelength range between 400 and 4000cm^{-1}. To show changes in the intensities of the transmission spectra of the aged and fatigued bitumens compared to the virgin sample, absorbance spectra (logarithmic representation of the absorbed infrared light of a sample) were generated and directly compared. Since the absorbance spectra are the sum of the individual spectra of the entire number of bitumen constituents, the evaluation can only be done qualitatively.

Figures 4 shows a comparison of the transmission and absorption spectra for the unmodified bitumen 50/70 in all three conditions, virgin, aged (RTFOT+PAV) and fatigued, within the wavenumber range 500-4000cm^{-1}.

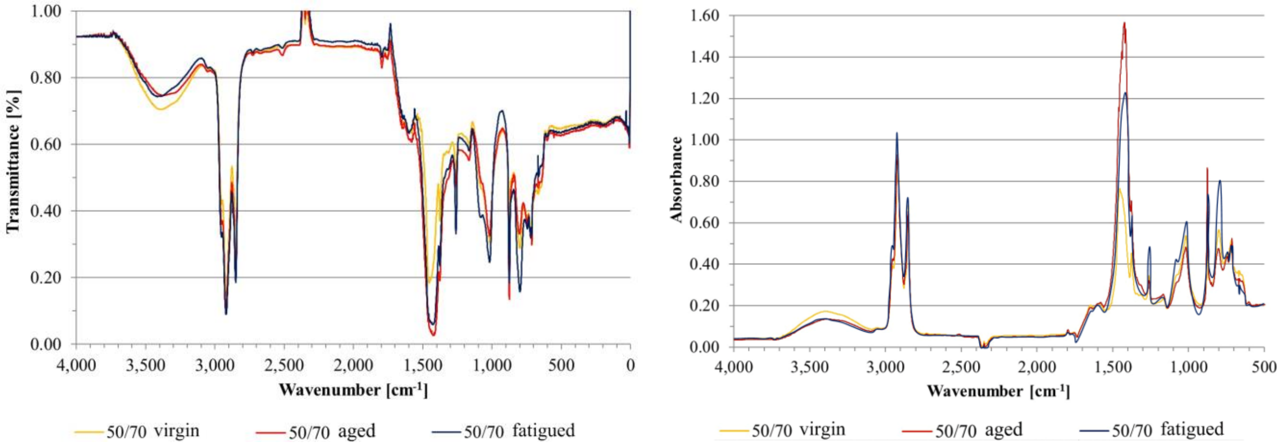


Figure 4: Transmission and absorption spectra for bitumen 50/70

Table 2 reflects the percentage changes in the transmissions of the aged and fatigued samples compared to the virgin bitumen. The functional groups that are linked to these wavenumbers are also listed. The determination of the functional groups for these wavenumbers was carried out according to the method proposed by Hesse et al. [24]. The spectra of the aged and fatigued bitumen sample indicate three areas of opposite changes in the transmission. Three decreases in the transmission wavenumber can be identified: ῦ=1425, ῦ=875 and ῦ=713 cm^{-1}.

Table 2: Percentage changes in the transmission of 50/70 bitumen and functional groups

Wavenumber ῦ [cm^{-1}]	Change in transmission [%]		Functional group
	Virgin vs. aged	Virgin vs. fatigued	
~713	- 18,7	- 6,5	Saturated hydrocarbons (alkanes) benzene rings
~800	+ 17,6	- 43,8	Unsaturated hydrocarbons (alkenes)
~875	- 61,1	- 46,2	C-C group (aromatics bonds)
~1020	+ 7,5	- 16,7	Ester- group
~1090	+ 5,2	- 18,7	Ester- group
~1260	+ 2,0	- 27,5	O-H- Group
~1425	- 89,3	- 74,3	C-H- Group

Similarly to the unmodified bitumen, transmission and absorption spectra were obtained for the polymer modified 25/55-55 A bitumen (Figure 5). The changes in the transmissions of the aged and fatigued material with respect to the virgin bitumen are reported in Table 3.

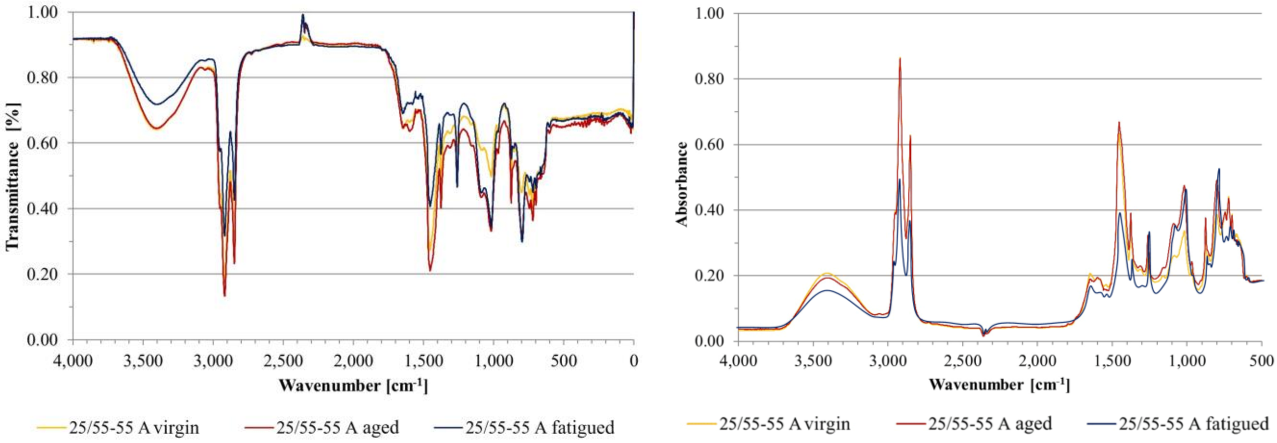


Figure 5: Transmission and absorption spectra for bitumen 25/55-55 A

Table 3: Percentage changes in the transmission of 25/55-55 A bitumen and functional groups

Wavenumber ῦ [cm^{-1}]	Change in transmission [%]		Functional group
	Virgin vs. aged	Virgin vs. fatigued	
~800	-41,3	- 27,5	Saturated hydrocarbons (alkanes) benzene rings
~875	-20,6	+14,8	Saturated hydrocarbons (alkanes) benzene rings
~1020	-33,9	-24,1	Ester- group
~1090	-25,8	-18,7	Ester- group
~1260	-20,6	-16,8	O-H- Group
~1380	-12,9	+34,8	O-H- Group
~1450	-24,1	+81,2	C-H- Group

The wavenumbers ῦ= 875, ῦ=1380 and ῦ = 1450cm^{-1} show opposing transmission changes for the aged and fatigued material. Consistent decrease in the transmission occurs for the following wavenumbers: ῦ=800, ῦ=1020, ῦ=1090 and ῦ=1260 cm^{-1}.

4.3 AFM analysis

In addition to the chromatographic and spectroscopic analysis of bitumen, AFM technique was used to evaluate the evolution of the surface structure across the three different material conditions: virgin, aged (RTFOT+PAV) and fatigued. The specimens were prepared by heating the bitumen and then pouring it into small moulds. In the case of the fatigued bitumen, the material was directly removed from the DSR plates and heating was avoided, to limit any possible further ageing effect. However, this resulted in a corrugated surface which was not sufficiently even to perform reliable AFM tests. Therefore, AFM measurements could be conducted only on virgin and aged bitumen.
An atomic force electron microscope (AFM) XE 100 from Park Systems was used for the measurements. The AFM device was located within an acoustic chamber in order to isolate the measurements from any potential vibration and noise coming from the surrounding environment. The topographic measurements were conducted in non-contact- mode. In this case the probe attached to the cantilever beam does not come into contact with the sample surface. A predefined area is scanned twice line by line. In addition to the topographical features, surface properties such as stiffness and adhesion can be determined. The AFM results are shown as topographic images of the surface. The scanning area for each sample of bitumen is 15 x 15 microns. Smaller materials areas with dimensions of 3 x 3 microns were also evaluated.
In Figures 6 and 7 the topographies of the 50/70 bitumen in virgin and aged conditions are presented together with the measurements of selected areas corresponding to specific protruding structures. These irregularly distributed structures, consisting of elevations and depressions, are commonly known as "bee structures".

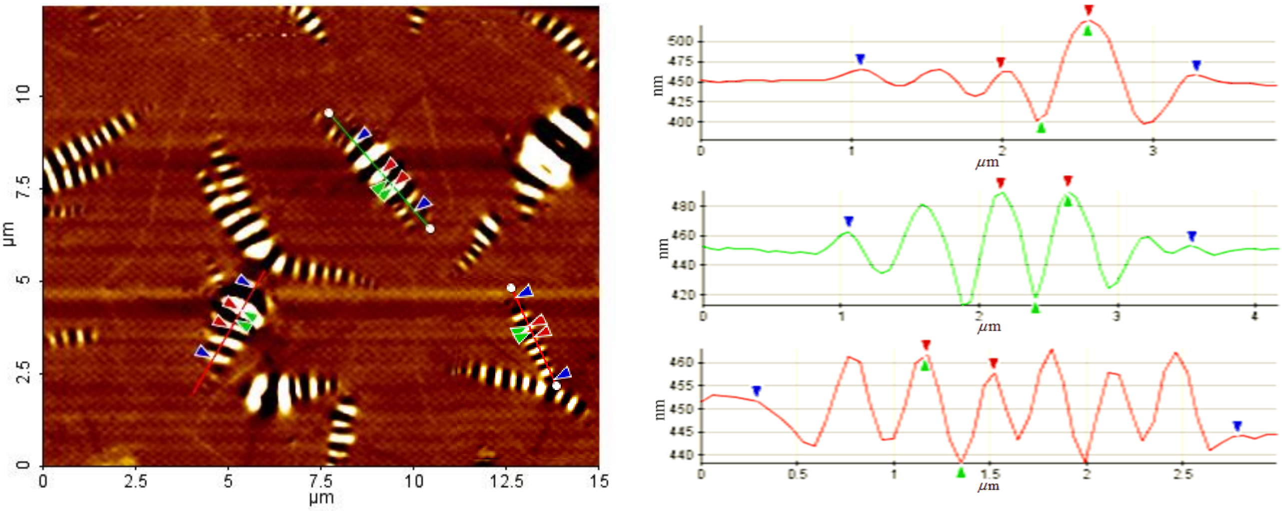


Figure 6: AFM topography for bitumen 50/70 - virgin

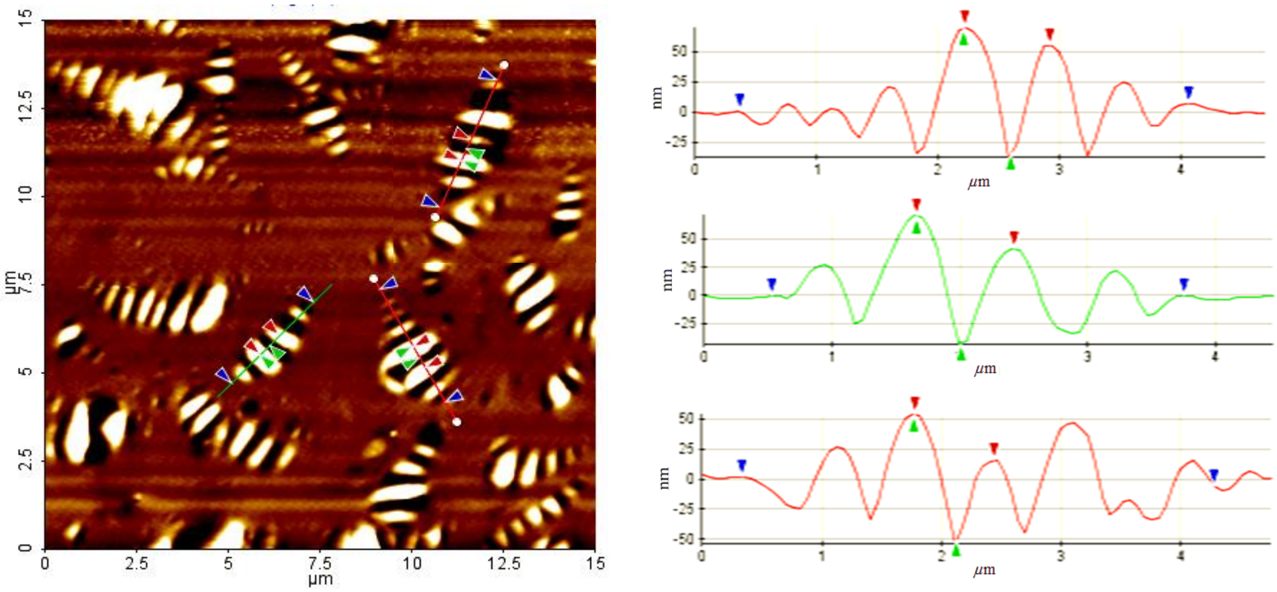


Figure 7: AFM topography for bitumen 50/70 – aged

The characteristic bee-structures are present in both virgin and aged bitumen. However, an increased number of these structures can be seen in the aged bitumen with larger spaces between the bands, increased distance between peaks and valley and with overall increased dimensions as shown in Table 4.

Table 4: Structural surface changes in bitumen 50/70 virgin – aged

Mean [nm]	50/70 virgin	50/70 aged	Difference virgin vs aged [%]
Band distance Δx (red markers)	500	703	+30
Height difference ΔH (green markers)	72	106	+50
Global length L (blue markers)	2401	3621	+50

The colour of the markers refers to Figures 6 and 7

A similar analysis was performed for the 25/55-55 A polymer modified bitumen (see Figures 8 and 9). Irregularly distributed structures can be observed on the surface with dimension significantly smaller than in the case of the unmodified bitumen. These structures present elevations and depressions of different degrees. In addition, the topography of the aged bitumen is similar to the one of the virgin sample where needle-like structures arise from the surface.

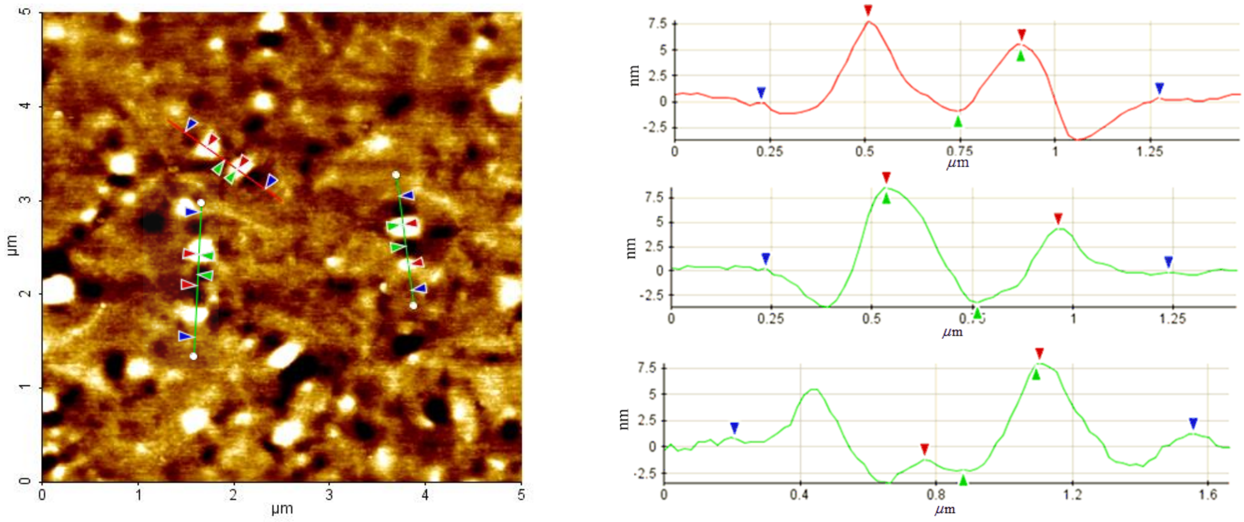


Figure 8: AFM topography for bitumen 25/55-55 A - virgin

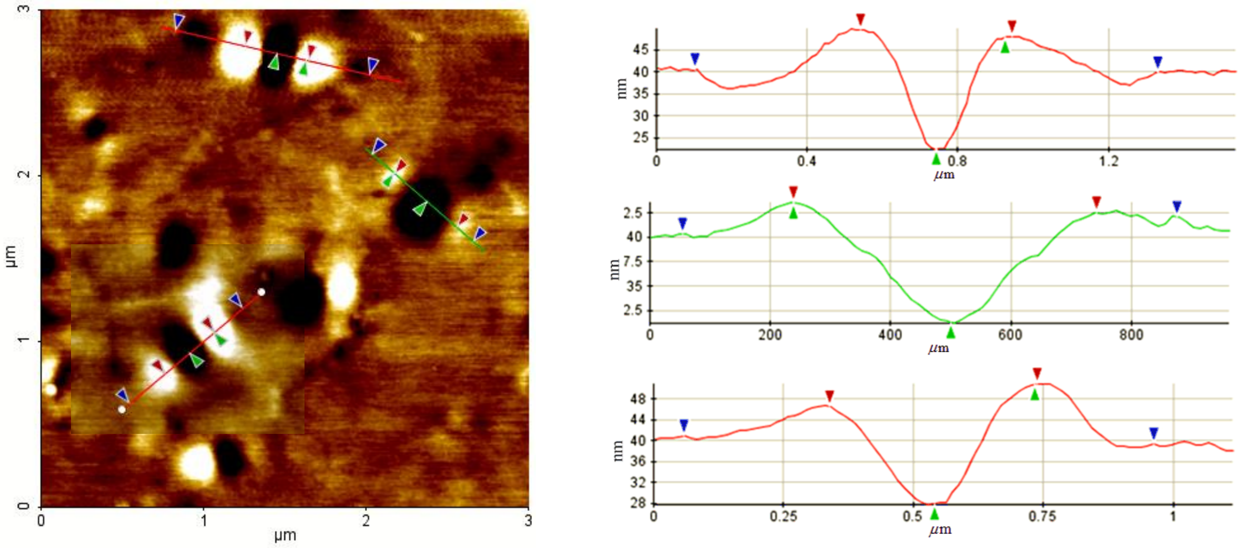


Figure 9: AFM topography for bitumen 25/55-55 A – aged

The distances between the elevations of the measured profiles are very different, while more consistent values were found for height and global length of the surface structures. Table 5 presents a comparison of the mean values of the bee-structures dimensions for virgin and aged bitumen. An overall increase of the bee-structure size is observed for the aged bitumen similarly to what was previously found for bitumen 50/70.

Table 5: Structural surface changes in bitumen 25/55-55 A virgin – aged

Mean [nm]	25/55-55 A virgin	25/55-55 A aged	Difference virgin vs aged [%]
Band distance Δx (red markers)	393	415	+ 5 %
Height difference ΔH (green markers)	9,47	15,95	+ 68%
Global length L (blue markers)	1133	1444	+ 30 %

The colour of the markers refers to Figures 8 and 9

4.4 Discussion of the results

The TLC-ID was used to separate the two bitumens into their four SARA fractions. A close look to the 50/70 bitumen indicated an increase in resins and saturated hydrocarbons in the transition from virgin to aged conditions. In the case of fatigued bitumen, significant changes were found only for resins. Small but consistent changes were observed for the polymer modified bitumen, with a decrease in the aromatics and resins, and an increase in the asphaltenes for aged conditions. Decrease of asphaltenes and resins coupled to an increase in the aromatics and saturated hydrocarbons was found for fatigued conditions. Although some changes in the proportions of the SARA factions could be detected, this is not sufficient to support the assumption of structural changes in the molecules. One of the reasons may be the fact that ageing was limited to the RTFOT procedure [21] for this type of test.

Infrared spectroscopy allows analysing bitumen changes in terms of transmission or absorbance spectra for certain wavenumbers. These changes are indicated by variation in the vibration of different functional groups. The results differ according to spectral comparison between the virgin and the aged or fatigued bitumen. Different wavenumbers were observed for unmodified and modified bitumens. These differences can be explained with various oil origin, different chemical compositions and polymer modification. Nevertheless, the quantification of the specific substances remains difficult since bitumen can contain numerous carbon compounds with chain lengths up to C^{150} atoms, which absorb infrared light. By elemental analysis, it is nevertheless possible to determine the proportions of C, H, S, etc. atoms. This can be used to restrict the possibilities at a specific absorbance level when determining functional groups.

In order to clarify the relationship between physical properties of bitumen and the surface structure, a microscopic analysis was performed with the AFM. Differences in the topography between the unmodified and the modified bitumens were observed. The surface of the 50/70 bitumen showed, both in virgin and aged conditions the characteristic bee-structures [10,25]. These structures increase by approximately 50% in height and length in the aged condition. This may be linked to the presence of larger amount of asphaltenes in the aged condition [26]. Significant differences in the shape of the bee-structures were observed on the surface of the modified bitumen, where needle-like structures are visible. In the aged sample, a significant increase in length (approximately 70%) of these needles was detected. In summary, it can be established that the surface structures can be potentially used to discriminate unmodified bitumen from modified bitumen, where the difference is most likely associated to the polymer modification.

5. CONCLUSIONS

In this paper, changes in the microstructure of one unmodified bitumen and one modified bitumen were investigated with three different experimental methods: thin-layer chromatography with flame ionization detection, Fourier Transform Infrared with attenuated total reflectance and Atomic Force Microscopy. Three material conditions were considered: virgin, aged and fatigued. Based on the experimental work performed in this research effort the following conclusion can be drawn:

- Chromatographic analysis showed that the approach is valid to explain structural changes by a proportional change in the SARA fractions. The interpretation of the results showed an opposite trend with respect to the simpler data obtained from the spectroscopic analysis. Therefore, based on the measurements conducted on the three bitumen conditions (virgin, aged and fatigued), the actual colloidal model appear to be consistent with the experimental findings. Nevertheless, the analysis was limited to short-term aged bitumen and, thus, additional tests on long term-aged material should be conducted to clarify the limited variation observed, and then further compared with the results of spectroscopy.
- The infrared spectroscopic analysis proved to be useful to identify structural changes of virgin, aged and fatigued bitumen samples. These structural changes corresponded to changes in intensity of transmission spectra due to increased or decreased molecular vibrations of functional groups in certain wave numbers. Nevertheless, a precise identification of the specific functional groups requires additional experimental investigation, since the vibration modes are due to the combined contribution of different functional groups.
- Based on atomic force microscope analysis, it was possible to detect structural changes to the surfaces of virgin and aged bitumen samples. A proportional increase of the characteristic bee-structures could be observed in long-term aged materials. The type and the shapes of the surface structures were different for unmodified and polymer modified bitumen. While a more regular shape could be observed for plain bitumen, a needle like topography was found in the modified material; this is most likely associated to the specific bitumen modification.
- All the selected analysis methods were able to discriminate the structural changes between different materials and conditions in the bulk and on the surface.

The results obtained in this research efforts are quite promising; however, additional experimental analysis and modelling, including alternative testing methods need to be explored to further improve our understanding of the microstructural changes of bitumen. This is especially important for design purposes, since the evolution of the microstructure directly affect the long term performance of the pavement. This is the objective of an on-going RILEM inter laboratory research project (task group CMB 252 on Chemo-Mechanical Characterization of Bituminous Materials) within which the Braunschweig Pavement Engineering Centre (ISBS) at the Technische Universität Braunschweig is currently active.

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