

Aging of Bituminous Films under Ambient Conditions Compared to Accelerated Aging in the Pressure Aging Vessel

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ABSTRACT

As binder aging plays a significant role in the durability and performance of asphalt pavements, it is important to understand and quantify the effects of aging. A first objective of this study is to compare accelerated aging versus aging under more realistic conditions. Bituminous binders were aged using various procedures, in a first procedure, binders were aged outdoors in such a way that a maximum exposure to direct sun radiation was obtained. In a second procedure, samples were also outdoor aged, but without direct exposure to sun radiation. In a third experiment binders were aged indoors at ambient conditions initially with exposure to sun radiation, and also without exposure to light (dark aging). Finally binders were aged in the pressure aging vessel (PAV) under standard conditions.

The samples were primarily investigated by Fourier transform infrared spectroscopy (FTIR), in attenuated reflection (ATR) mode. This technique is an excellent tool to investigate surface characteristics, since the infrared radiation is only penetrating two to three micrometer under the surface, which is in contact with the measurement cell. With FTIR-ATR, the bottom as well as the top surfaces could be investigated rather easily. For some of the binders, the depth of aging was further evaluated using a macrotome to slice the aged films. The macrotome was also used to collect enough surface material, to evaluate the aging with gel permeation chromatography (GPC).

As expected, and as is known in literature for a long time, under field conditions bitumen ages more severe at the top surface compared to the bottom surface. The tests for the samples aged under ambient conditions show that bottom surfaces were almost unchanged, while top surfaces showed significant changes in the spectrum, with the formation of a lot of polar groups. On the other hand, for the samples aged in the PAV, the aging was rather homogeneous through the thickness of the binders and the changes in the spectrum due to aging were much smaller. The amount of carbonyl groups after PAV aging at 100°C, 20 hours, is identified on the surface of samples aged at ambient temperature already after a few days. The tests also show clear differences in the FT-IR spectra, depending on whether the binders were exposed or not exposed to sun radiation. The dark aged binder surface (no exposure to light, only to air) also changed with time. In this case, the formation of alcoholic functional groups was quite clear, with almost no formation of carboxylic groups.

Keywords: Aging, Pressure Aging Vessel, FTIR spectroscopy, Gel Permeation Chromatography, aromaticity

1 INTRODUCTION

In literature several investigations have shown the importance of binder aging in relation to the durability and performance properties of pavements [1, 2]. For example in ref 1, cracking, in particular top-down cracking, was associated with age hardening of the binder. In ref 2, a porous asphalt, containing different sections was investigated, and extensive ravelling and loss of chipping was observed for those binders that showed extensive age hardening.

When studying binder aging, it is very common to use accelerated aging tests, since in this way large amounts of homogeneously aged material can be obtained, to be applied in the tests method of choice. A concern that remains is, if the acceleration, which is almost always achieved by increasing the temperature, could change the aging mechanism, and possibly lead to other reaction

products compared to field aging. Alternatively, aged binders can be recovered from asphalt cores with a known service life. In this case, it is also possible to recover as a function of depth, due to practical reasons depths are in the range of several mm thickness [3,4]. In ref 3 for example it was observed that for a dense graded asphalt, only the top 3mm of the asphalt showed effects of aging, lower layers were not influenced. However, concerns about the recovery process when following this procedure remain; is the recovery process altering the properties and is the recovery complete. Occasionally, bitumen films have been naturally aged [5] or by means of weathering ovens [6], and effects of UV radiation have been reported.

Physical / rheological changes after aging, are well documented in literature [5-8], almost always the binder hardens, and shows an increase in elasticity. Regarding chemical changes, infrared spectroscopy always reveals an increase in carbonyls, C=O containing functional groups, and in sulfoxides, S=O containing groups.

In this project, bitumen films were aged under realistic conditions, and the investigations were conducted without re-homogenizing the samples. The influence of sun radiation and exposure to light were investigated. This more natural aging was compared to an accelerated aging using the pressure aging vessel (PAV).

2 EXPERIMENTAL

2.1 Materials

Several binders were investigated, but the results in this paper will focus on one binder, an unmodified paving grade (pen 100 dmm, R&B 43°C). This binder is referred to as B100.

2.2 Aging procedures

Initially, binders were aged in the PAV, using standard conditions (100°C, 20h, 2.1MPa air pressure). In addition, binder films, with a thickness variation between 0.3-0.5mm, were left outside for a period of 1 year (April 2010 to April 2011). One set of films was exposed as much as possible to direct sun radiation, while a second set was never directly exposed to sun radiation, these samples will be referred to as sun and shadow samples respectively. In figure 1, pictures of the bitumen films, after 1 week, and after 1 year are shown.



Fig. 1: Photographs of the outdoor aged binder films (left: after 1 week, right: after 1 year)

In figure 2, average monthly temperatures for the period of interest are shown, as well as the number of sunny hours per month. It can be observed that the climatic conditions in this area are quite mild.

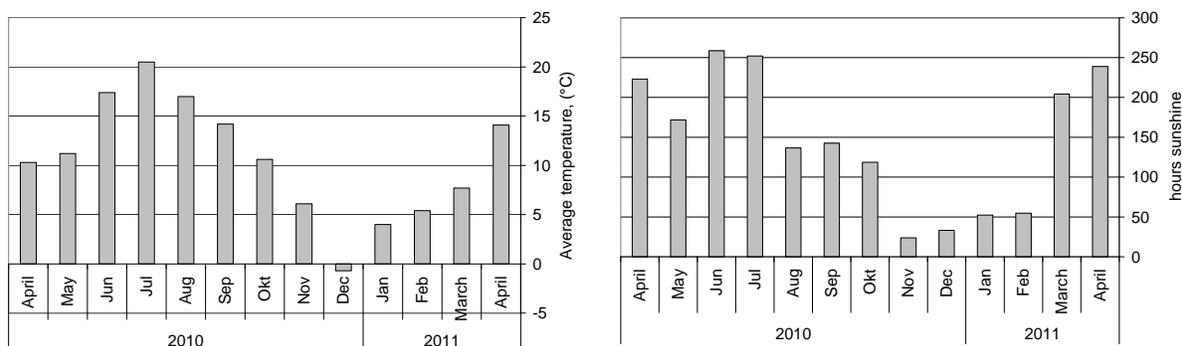


Fig 2. Overview of average monthly temperatures, and number of sunny hours during the outdoor aging period

Furthermore, bitumen films were also placed indoors, still with exposure to sun radiation, but filtered through a glass window. In this way, dust collection, and influences of rain on the surfaces was avoided. For this set of samples the aging was followed as a function of aging time. Finally, the aging of a sample was also followed under ambient conditions, with exposure to air, but without exposure to light (dark aging).

2.2 Test methods

The main test method to evaluate chemical changes during aging was Fourier Transform Infrared Spectroscopy (FTIR), combined with attenuated total reflection (ATR). This technique is in fact a surface characterization method, because the infrared beam is only penetration 2 to 3 micrometer in the sample. The exact penetration depth is dependent on the wavelength, on the refractive index of the material to be investigated, and the type of prism used. Moreover, sample pretreatment is unnecessary. But, in order to make quantitative comparisons it is necessary to obtain a good contact between sample and prism. For bitumen binders this causes normally not a problem, in this case the binder films were pressed cold to the prism of the ATR measuring set-up. The instrument used was a Nicolet IS 10, with a diamond cell (smart-orbit)

Another characterization method is Gel Permeation Chromatography (GPC), in this test the binder is first dissolved in a solvent (THF in this case). Then the solution is eluted through a porous column and is separated according the volume of the molecules, larger molecules elute faster compared to smaller molecules. The concentration of substances in the eluent is continuously monitored using UV-visible light absorption (UV-vis), a wavelength variation from 200nm to 800nm is possible. The specific instrument used was an Alliance 2690 Separator module, with a PDA detector 996, 3 Jordi columns, the injected volume was 20 μ l, sample concentration in THF was between 0.6 and 1 mg/ml.

On some of the binders, macrotome cuts were made, and these slices were further investigated using a FT-IR microscope. These tests were conducted by a service lab, Anfers, located in Louvain la Neuve, Belgium (www.ansers.eu) The macrotome was a Reighert macrotome, and the FT-IR microscope was a Bruker Equinox 55, combined with a FT-IR Hyperion microscope.

Only the samples aged in the PAV could be evaluated with other tests like for example rheology and viscosity.

3 RESULTS

3.1 Infrared investigations

In figure 3, several FT-IR spectra are shown. In the upper figure the samples aged outside are shown. It is obvious that the bottom side of these bitumen films are almost not aged while the top surface shows some extreme changes. A lot of polar compounds are formed during this aging, this is obvious from the spectral region 3500-3000 cm^{-1} , which is characteristic for an OH stretching of groups that form hydrogen bonds. If derived from alcohols the range is 3500-3200 cm^{-1} , if derived from carboxylic acids the range is 3300-2500 cm^{-1} , in this case probably a combination of both compounds is present. Another important change related to the formation of more polar structures is observed at 1700 cm^{-1} , a region characteristic for C=O groups. Many molecules contain C=O groups, carboxylic acids, ketones, aldehydes, esters, anhydrides, each with characteristic wavelengths, but in this case the signal is too broad to assign it to certain specific functional groups. Furthermore, strong changes are seen in the region 1340 cm^{-1} to 910 cm^{-1} , this region could be assigned to a C-O stretch, if these are derived from carboxylic acids a strong signal is expected in the range 1320-1210 cm^{-1} , if derived from alcohols the (rather strong) C-O stretch would fit in the range 1260-1000 cm^{-1} , depending on the type of alcohol. In literature the signal at 1030 is almost always assigned to the formation of S=O groups. Another clear change is seen in the region 2960-2850 cm^{-1} , this region is typical for CH₂ and CH₃ stretching, of saturated compounds, and there is a clear decrease in the number of these compounds. As these samples were stored outside, the surface could also contain some water, therefore the water spectrum is added in the graphs, on the same scale. The shadow sample could contain some water, (characteristic signal at 1643 cm^{-1}), but still many of the observed signals are not related of water.

In the second graph, from the top, spectra before and after PAV aging are shown. In this case top and bottom side of the aged binder were equal, (this is not shown in the graph) so the sample is aged quite homogeneously. Probably, as the binder has a low viscosity under these aging conditions, convection and re-homogenization can take place during the test. The changes observed after PAV aging are minimal compared to the changes observed in the previous graph. There is some change in the 1700-1500 cm^{-1} region, in the 1030 cm^{-1} region and also a very minor, but consistent, increase in the -OH hydrogen bonding region (only visible at higher magnifications, not on this graph).

In the third graph, spectra from binders aged indoors, with exposure to sun radiation (behind glass) are shown. By doing so, the accumulation of dust and the influence of rainwater, which could possibly interfere with the samples aged outdoors, was avoided. The time evolution shows that the oxidation happens rather fast, the sample aged indoors after 65 days showed larger signals than the ones aged outdoors for 1 year. There is no explanation yet, but probably dust prevented or slowed down the oxidation of the sample stored outdoors, alternatively, it could be that the surface has become so polar, that water soluble compounds are formed, which are then washed away with precipitation. This will be investigated in a next stage of the project. But more importantly, the changes observed after indoor aging are rather similar to the ones observed during outdoor aging.

Finally in the last graph, the binder before and after dark aging (still ambient) is shown. Of course now, the aging is rather slow, and only after one month, changes start to become visible. This sample clearly does not show an increase in the carbonyl region, in contrast to the other procedures. This indicates that carbonyls are mainly formed with exposure to (sun)light, or to a lesser extend also if temperature is high enough (like in the PAV at 100°C). During dark aging hydrogen bonding becomes visible, which is, in this case most likely due to the formation of alcohols, as there is no carbonyl formation. If alcohols are formed there should also be a rather strong C-O stretch (1260-1000 cm^{-1}). Therefore, the signal at 1030 cm^{-1} could also be related to the alcohols that are formed, and maybe not because of sulfoxides. But this needs further confirmation.

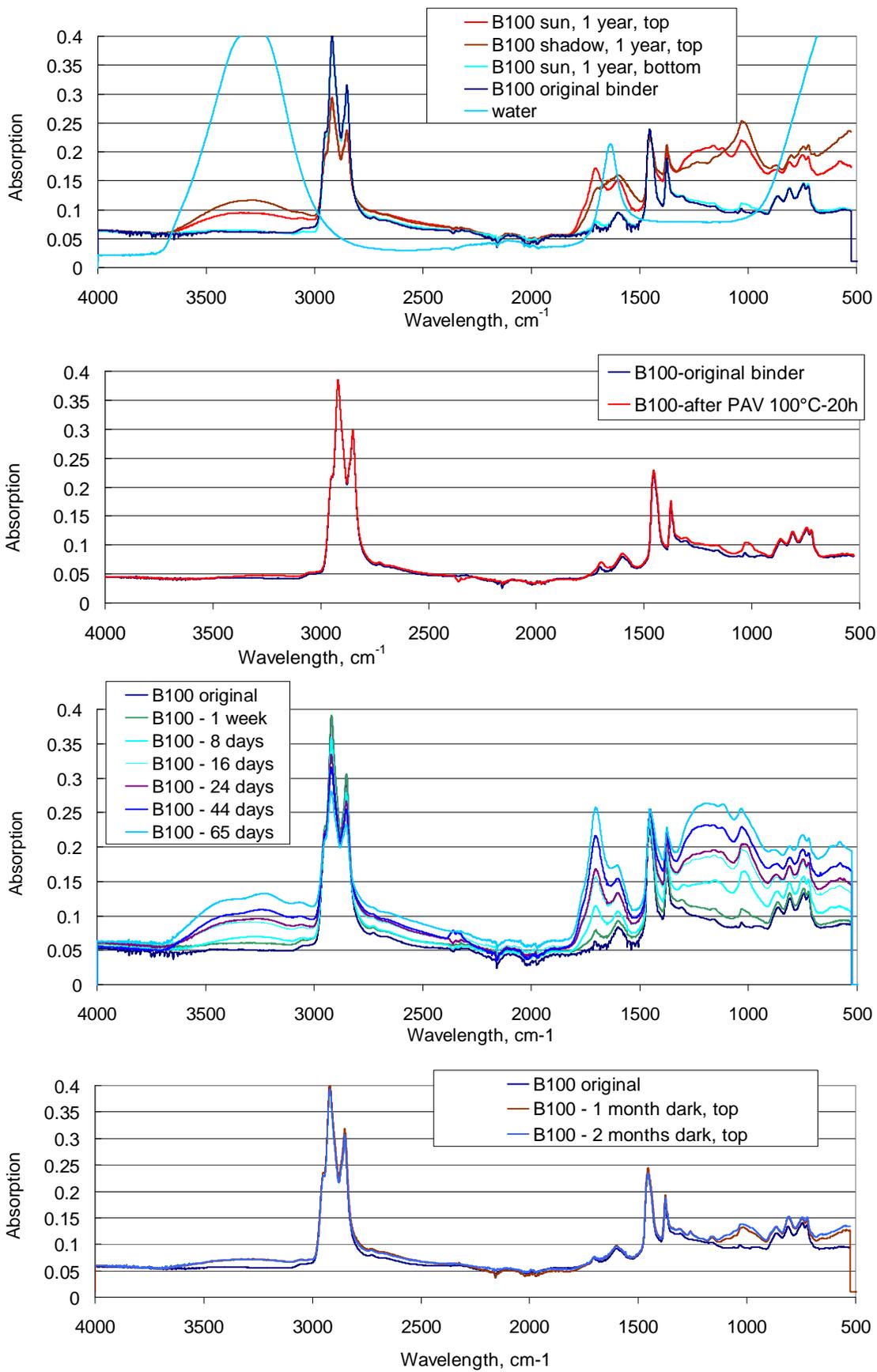


Fig. 3: FT-IR spectra before and after various aging procedures, one binder, same scales.

In figure 4, time evolutions of several peak heights with time are shown. Only 4 peak positions were chosen, since for many signals like for example the signal at 1600 cm⁻¹, which is associated to an aromatic C-C ring vibration, it is not clear to what extent this signal itself is increasing, or if it is only changing because other nearby signals, in this case the C=O one, are changing. In figure 4, the corresponding heights after PAV aging are also shown, and it is quite obvious that the changes after PAV are very minor in this graph. The C=O absorption reached after PAV 100°C 20 hours is lower than surface aging at ambient temperature after 5 days.

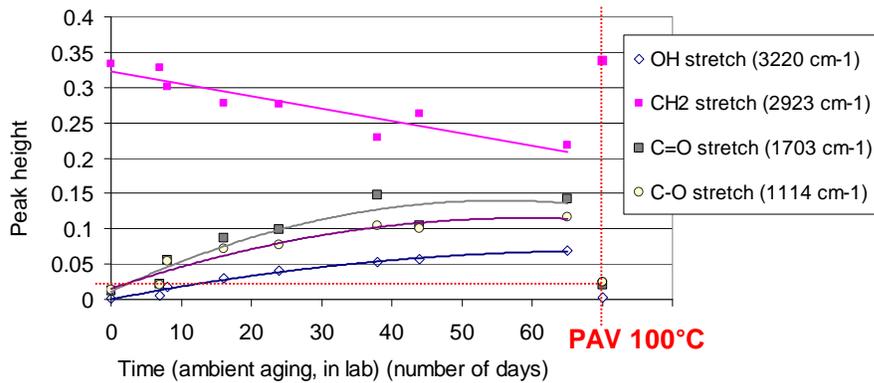


Fig 4: Time evolutions of several selected FT-IR peak heights of the samples aged indoors with sun exposure. The corresponding heights for the PAV aged binder are also indicated.

3.2 Macrotome investigations

Some of the binders were analyzed further, to investigate how deep the oxidation process has continued, or how thick the oxidized layer is. Initially a rather simple approach was used: in fig. 5, a microscopic picture through the thickness of the binder film is shown, the top part is the oxidized layer, while more in the bottom, the black layer is the (rather unaffected) bitumen layer, and below this the bright part, is aluminium foil, which was used as a support for the binder films. This picture shows a color difference between the oxidized and the bottom layer. Just based on this color change, the oxidized layer has a thickness of about 120 to 130 μm .

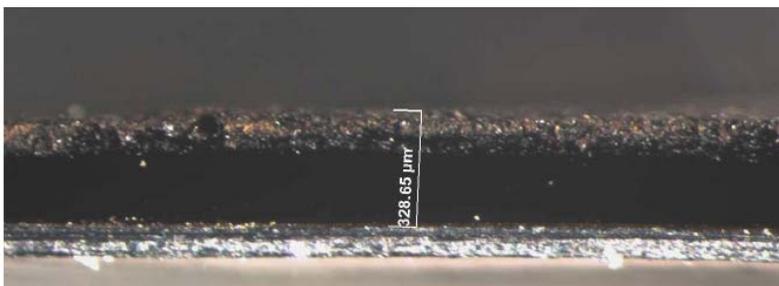


Fig. 5: Microscopic picture through the surface of a sample, aged for 1 year, outdoor with sun exposure. The upper side of the figure is oxidized, in the bottom part, the aluminium foil, used to support the binder films is visible (bright part.)

Using the macrotome, a small slice (80 μm thick) was cut through the thickness of the binder film. And subsequently this slice was further cut in small pieces that were investigated in the FT-IR microscope. A problem was that the small slice elongated during further handling which gives

some uncertainty to relate distances back to the initial thickness, therefore only thickness ranges are reported. In figure 6, FT-IR spectra related to several depths are presented. There is no effect of oxidation for layers below 130 μm , from the surface, this corresponds to the color change. For thicknesses smaller or equal to 30 microns from the surface, the C=O signal is quite large, for intermediate thicknesses there is some effect but small.

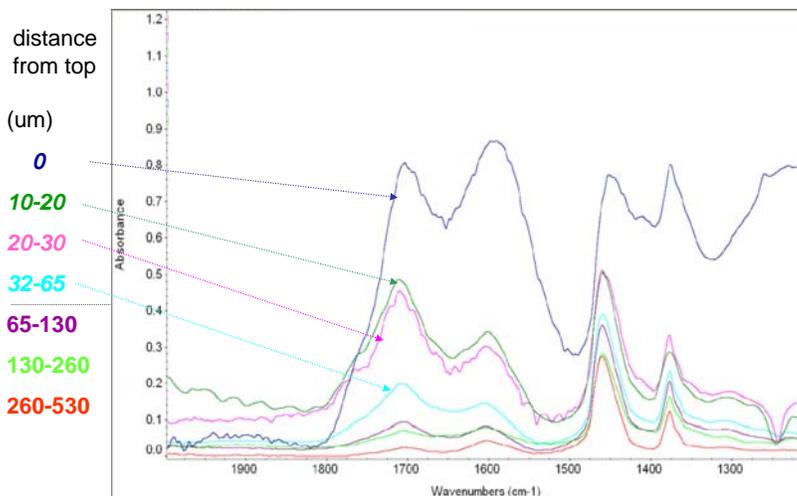


Fig. 6: FT-IR scans recorded as a function of the distance from the oxidized surface.

3.3 Gel Permeation Chromatography

Gel Permeation Chromatography, GPC, was used to evaluate the binders. In these tests it was necessary to dissolve some material in a solvent. First the experimental conditions were adapted so that tests could be performed on samples down to a sample size of 1mg. For those samples that aged mainly at the top surface, the macrotome was used to collect as much as possible material from the oxidized layer (up to 130 μm). For the sample aged in the PAV, this was not an issue since aging was rather homogeneously.

GPC separates the components according to their hydrodynamic volume in the selected eluent (THF in this case). A relationship between volume and molecular weight is assumed. If one type of chemical substance is investigated for example polymer chains of various lengths, this assumption is valid. However for bitumen, with a large number of chemical species, the volume is also a function of solubility, components that are on the edge of being soluble may easily form associations, which will be seen as larger species. On the other hand some components may also have interactions with the column material, this will lead to longer retention times, and apparent lower molecular weights. And finally the relation retention time versus molecular weight is established using polystyrene standard, so for bitumen the numbers can only be used in a relative way. To monitor the concentration of the solution when it is separated on the GPC column, UV-vis absorption was used. And again for components of one chemical type, there is a direct, mostly linear relation between absorption and concentration. But for different molecular species this is not valid anymore, since each component has its own specific absorption coefficient, to influence the spectrum. Therefore GPC on bitumen should be interpreted with care.

In fig. 7 two examples of a GPC scan are shown, the X-axis represents the retention time, the Y-axis the UV-vis wavelength (starting at 200nm to 800nm) and the Z-axis is the amount of absorption. Currently, it is not possible to evaluate absorption versus retention time, it is only possible to measure a total (summation of all retention times) absorption per wavelength. The sharp small signal at long retention times indicates the end of the measurement and is not related to the

bitumen sample. Qualitatively, one can see that there is more elution at shorter retention times after aging, indicating maybe larger structures or components that form associations. Calculated molecular weights (with error bars, derived from the standard deviation) are shown in figure 8. It can be seen that for all aging procedures there is an increase in the “apparent” average molecular weight, differences between the aging tests cannot be distinguished.

Regarding the UV-vis absorption, normally if conjugated structures become larger, the UV-vis absorption shifts to longer wavelengths (or lower energy levels). So in order to check if there was a change in this parameter the UV absorption at longer wavelengths 380 to 610 nm was checked and this is also shown in figure 8. In this case the absorption is normalized to account for slight variations in the concentration of the THF solution. This bar diagram indicates that only after PAV aging there is an increase in this parameter, but for the samples aged at ambient conditions, the absorption is about similar as for the original sample (the error bars overlap). An increase in aromaticity can in principle also be observed using the FT-IR spectra, especially the region 1500-1600 cm^{-1} , which is related to a C-C aromatic ring vibration or to double bonds. After PAV aging there is a small increase in this absorption, but after outdoor aging, or ambient aging in the lab, the increase in the 1700 signal is so dominant that it is not clear if there is also a change in the 1600 region.

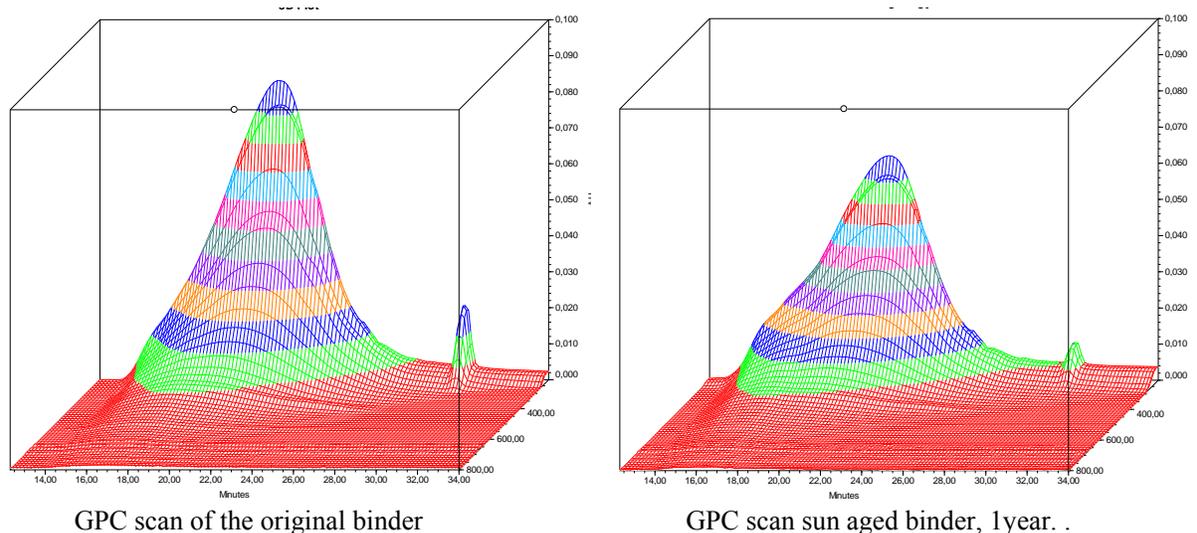


Fig. 7: Examples of GPC scans, (scales are the same in both graphs)

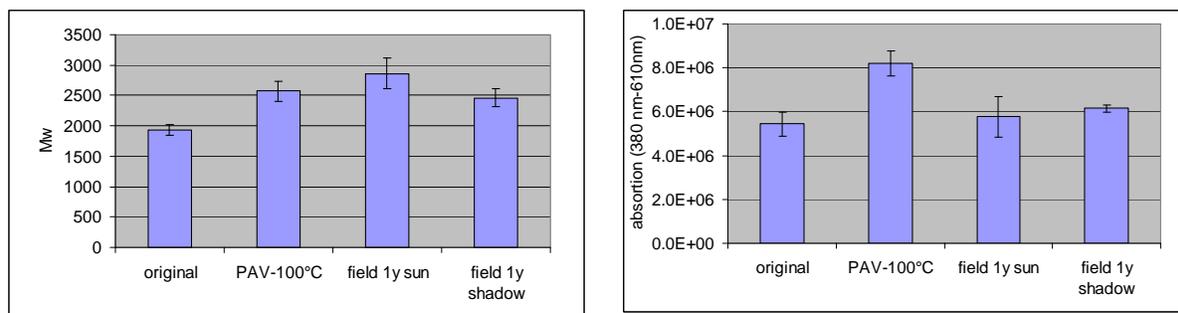


Fig 8: Calculated weight average molecular weights (left figure) and UV-vis absorption (right figure) before and after various aging procedures. Field aged samples contain only the top 130 μm part.

3.4 Other investigations

For the sample aged in PAV, it was possible to conduct more tests: In fig 9 stiffness measurements (at a frequency of 1Hz) as a function of temperature are shown before and after aging. It is quite clear that the stiffness increases and this effect is larger at higher temperatures. A similar tendency was found for the phase angle, in fact these changes are well-known and described in literature.

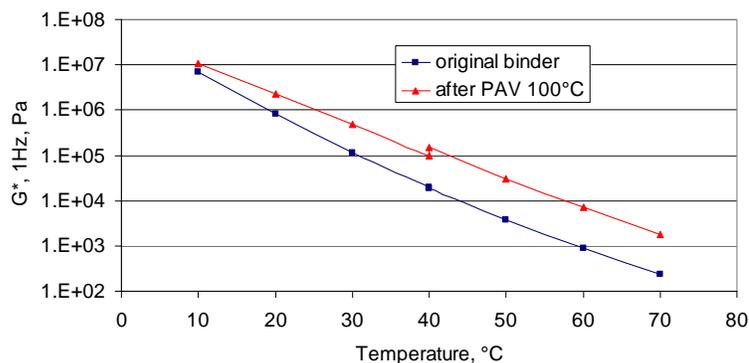


Fig 9. Stiffness (G^* at 1Hz) as a function of temperature, before and after aging in the PAV (standard conditions)

4 CONCLUSIONS

This study shows that after rather realistic aging conditions, a lot of polar components are accumulated at the surface of binder films. A time evolution demonstrates that this happens rather fast, and macrotome measurements as well as colour changes show that the oxidized layer is thin (120-130 μm at maximum). The polar compounds consist of carbonyl containing groups and compounds able to form hydrogen bonding. And there is also a clear reduction in saturated CH_2/CH_3 bonds. The tests also show that in the absence of light and under ambient conditions no carboxylic and mainly alcoholic groups are formed. Furthermore sun radiation seems to promote carbonyl formation.

The effects of ambient aging, at the surface, are much larger as what is obtained in a standard accelerated aging test (PAV in this case). The amount of carbonyls formed in the PAV is reached after a few days on the surface of ambient aged binder films. On the other hand, in the PAV, the binder is aged homogeneously through the film thickness. There are furthermore indications that condensed polyaromatic rings are preferably formed after PAV aging, and no clear indications of polyaromatics were seen after aging under ambient conditions.

5 OUTLOOK

It can be expected that the formation of a rather polar layer on the surface may influence the interactions, especially with other polar components (like for example stone material and water), and this certainly needs further investigation. Also the formation of polyaromatics, which have strong dispersive interactions, are expected to influence interactions and performance properties. Therefore in future studies we will investigate whether the observation that these are formed more after PAV aging and not in field aging, is general and applicable to more bitumen types.

And finally, if field behaviour, in particular traffic loading is considered, the formation of a thin and strongly oxidized top layer during service life is expected to play a role in the stress distributions and the sensitivity for crack initiation.

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