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Weathering Degradation Effect on Chemical Structure of Asphalt Binder

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Abstract: The room temperature and solar radiation are aggressive elements during service life of pavements which promote ageing effects on the bituminous binders. In an earlier work, the binder samples aged for 150 hours in a weathering chamber, which includes the effect of temperature and solar radiation, showed a behavior characteristic of full degraded samples in rheological tests. The objective of this study is to investigate the chemistry of the bitumen sample aged for 150 hours by using techniques such as coupled thermogravimetric analysis and mass spectrometry (TGA-MS). Elemental analysis indicated that a binder dehydrogenation occurs at 50 hours of weathering ageing, and that the oxygen/carbon ratio did not increase after 100 hours of ageing. The results of TGA-MS indicated that the size of hydrocarbon molecules present in asphalt composition increased with the ageing process. The binder samples before the weathering ageing released twice the hydrogen content than the samples aged for 150 hours, which released a higher content of oxidized fragments. The total ion current curve of the sample before weathering ageing decreased continuously with the increase in temperature, and the sample aged for 150 hours in the weathering chamber showed a sharp decrease of the total ion current curve at 400^{o}C.

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***Key words**: Ageing; Amorphous materials; Fourier transform infrared spectroscopy (FTIR); Oxidation; Thermogravimetric analysis (TGA).*

Introduction

The ageing performance of bitumen and its preventive measures have attracted more and more attention all over the world [1]. Bitumen ageing is one of the main causes of the degradation of asphalt pavement. In bitumen ageing, two mechanisms are involved: chemical changes in binder (irreversible) and physical hardening (reversible). The former involves processes of oxidation [2], loss of volatile components from bitumen, and exudation [3], and the latter may be attributed to the molecular reorganization to approach the highest stable thermodynamic state under a specific set of conditions [4].

Oxidative ageing causes hardening of bitumen and, consequently, the degradation of asphalt pavements. One of the main causes of bitumen ageing and embrittlement in service is the atmospheric oxidation of asphalt binder molecules with the formation of highly polar and strongly interacting functional groups containing oxygen.

In pavements, bitumen is exposed to ageing processes during storage, mixing, paving, compaction, and service life. Field ageing is a combination of traffic conditions, ultraviolet radiation from the sun, and moisture from rain and melting snow.

Although physical tests such as penetration and ring and ball tests proved sufficient for specification purposes until the development of modern polymer modified bitumen, the use of other tests that could measure important features of bitumen rheology became necessary, such as the susceptibility to loading stress, loading time, and temperature. In literature, physical parameters and the Fourier Transform Infrared analysis are used to evaluate the bitumen thermal and UV ageing [1]. The study of the chemistry of aged bitumen constitutes a gap in literature. Literature reports the effect of ageing on bitumen chemistry by using tests such as infrared spectroscopy, chromatography, and dynamic mechanical analysis [5]. Size-exclusion chromatography, thermal analysis (DSC, TGA), Fourier Transform Infrared Spectroscopy, and X ray diffraction were used to evaluate cross linking which occurs by bitumen irradiation [6]. In order to obtain information on bitumen chemistry, before and after Pressure Aging Vessel testing, n-heptane precipitation (Standard NF EN 12591), IATROSCAN chromatography (coupling between a thin-layer liquid chromatography on a silica gel and a flame ionization detector), FTIR spectroscopy and Differential Scanning Calorimetry (DSC) are used [4]. Size exclusion chromatography under high-speed conditions (HS-SEC), which yields information relative to asphaltene associations, was also introduced [4]. The coupling of IATROSCAN chromatography and n-heptane precipitation made it possible to identify and quantify polar resins [4]. Isacsson and Zeng [7] measured the chemical characteristics of the binders using Thin Layer Chromatography (TLC) and Gel Permeation Chromatography (GPC).

In an earlier work [8], the binder samples aged for 150 hours in a weathering chamber had a high brittleness and showed a behavior in rheological tests characteristic of bitumen with a highest degree of degradation. The objective of this study is to investigate the chemical characteristic of the bitumen sample aged for 150 hours in the weathering chamber using techniques such as coupled thermogravimetric analysis and mass spectrometry (TGA-MS). In order to simulate in-service ageing of binders, samples of a conventional binder 50/70 were submitted to the Rolling Thin Film Oven Test, RTFOT, to simulate mixing ageing, and then were tested

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by using the weathering chamber to simulate in-service ageing. The ageing properties of an asphalt binder were also evaluated by using dynamic mechanical analysis and Fourier Transform Infrared Spectroscopy.

TGA-MS analysis allows the detection in real time of the gaseous species released during thermal decomposition of solid samples. When gaseous species are simultaneously released, their correct identification may be difficult as the recorded mass spectrum shows the fragmentation pattern sum of all the species [9]. References were not found on characterization of asphalt binder by TGA/MS. However, TGA/MS is a very useful method applied in this work to evaluate asphalt binder after ageing by the release of molecules and hydrocarbon fragments during thermal decomposition. In our previous published work [10-12], the chemistry of asphalt binder was not studied and correlated with the weathering degradation process of asphalt binder as in the present paper.

Material and Methods

Granite plates of 150mm in length, 80mm in width, and 20mm in thickness were coated with 0.6 mm film of 50/70 asphalt binder, named CAP, after the RTFOT testing. Table 1 shows properties of 50/70 asphalt binder. The granite plates coated with the asphalt binder were tested in the Q-Sun Xe1 weathering chamber, according to the ASTM D-4798 (2008) Standard, in cycles of 80 minutes, which consisted of 64 minutes of light, and 16 minutes of light and water. The specimen temperature was 60^{o}C, and the irradiation was at 340 nm = 0.35 W/m^2. Variable power from 3500 to 6500 W maintained the intensity of irradiation. The samples were tested for 50, 100, 150 and 200 hours.

The FTIR spectroscopy was performed using the equipment ABB Bomem, model MB series of LEC-UFMG, and spectra were obtained, in units of absorbance in the range of 4000-400 cm^{-1}, recorded with 16 accumulations of reading, and resolution of 4 cm^{-1}, over a diamond cell.

The spectra, after application of baseline correction (nonlinear), were normalized and the ratios of intensities of the bands of νCH_2 (1455 cm^{-1}), νCH_3 (1376 cm^{-1}) and $\nu C = O$ (1703 cm^{-1}) were used to assess ageing.

The FTIR spectrum has characteristic absorption bands of bitumen. The carbonyl index was calculated by the measured areas between valleys. The choice of areas, rather than the heights of the bands, is due to the vibrations of the same type, which are simultaneously taken into account (C = O vibrations of ester, ketone and acid are between 1753 and 1635 cm^{-1}).

Since the film of bitumen does not have the same thickness, the spectrum can be brought to the same series of absorption for comparison [2]. The carbonyl index ($I_{C=O}$) was calculated by dividing the area of the carbonyl band centered around 1700 cm^{-1} by the area of the CH_2 band centered around 1455 cm^{-1} coupled with the area of the CH_3 band centered around 1376 cm^{-1} [13].

The coupled thermogravimetric analysis-mass spectrometry (TGA-MS) was performed in a NETZSCH model STA 449 F3 equipment. Samples of 20 mg of binder were analyzed under a flow of argon in the purge and protective, both in flow of 20 mL / min. The heating rate was up to 900°C at 10°C/min.

The elemental analysis was performed in a Thermo Finnigan equipment, Flash EA 1112 model, CHNS series.

It is noteworthy to mention that the samples analyzed by rheological tests were not submitted previously to RTFOT (Rolling Thin Film Oven Test), in opposite of the samples studied by FTIR, TGA/DTGA/DTA and TGA/MS. The Rolling Thin Film Oven Test was implemented in order to simulate the ageing due to a mixing process.

Results and Discussion

The carbonyl index of the asphalt binder during the ageing process was obtained by FTIR spectroscopy and is shown in Fig. 1. The carbonyl index increases as the weathering ageing time increases, tending to stabilize after 100 hours of ageing. However, two peaks of maximum values of carbonyl index were identified: one at 40 hours of testing in the weathering chamber and the other at 150 hours of testing in the weathering chamber as shown in Fig. 1. The mechanism of bitumen oxidation is very complex. Oxidation of methylene and degradation of unsaturated chains and or naphthenic

Table 1. Properties of 50/70 Asphalt Binder.

Property	Method	Result	Unit
RTFOT Mass Variation	D 2872	-0.182	%
RTFOT Ductility at 25^{o}C	D113	> 150	cm
Thermal Susceptibility Index	X 018	-1.1	
Solubility in Trichloroethylene	D 2042	99.9	% wt.
Softening Point	D 36	49.8	^{o}C
Penetration	D 5	54	0.1 mm
RTFOT Increase in Softening Point	D 36	3.9	^{o}C
Flashpoint	D 92	328	^{o}C
Brookfield Viscosity 135 ^{o}C-SP21 RPM	D 4402	337.5	cp
RTFOT Retained Penetration	D 5	57	%
Ductility at 25^{o}C	D 113	> 150	cm
Brookfield Viscosity 177^{o}C SP21	D 4402	62,64	cp
Relative Density at 20/4^{o}C	D 70	1004	-
Brookfield Viscosity 150^{o}C SP21	D 4402	168,6	cp
Rotational Viscosity at 60^{o}C	D 4402	2060	p

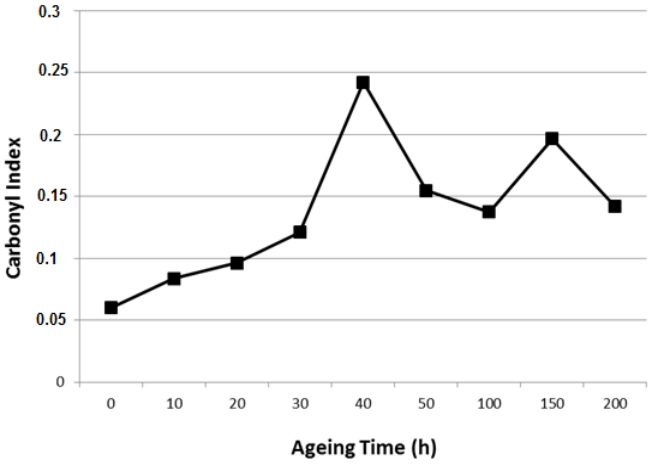

Fig. 1. Carbonyl Index for the 50/70 Asphalt Binder after RTFOT and Aged in a Weathering Chamber up to 200 Hours.

rings of benzene systems lead to ketones and carboxylic acids, increasing the carbonyl index [5]. In addition, aromatization and chain scission may occur during oxidative ageing [5]. When chain scission occurs, the content of CH_3 increases. The carbonyl index actually serves to track the polarity increase in bitumen. An increase in bitumen polarity also leads to a subsequent greater molecular association [4]. Thus, the chain scission mechanism dominates at the peaks of maximum of carbonyl index at 40 and 150 hours of ageing, increasing the polarity of bitumen. A greater fragmentation of molecules provides a higher oxidation rate, generating ends of carboxyl groups, and a subsequent maximum molecular reactivity and association occurred after 40 and 150 hours of bitumen testing in the weathering chamber.

The elemental analysis of the asphalt binder aged at different times (Table 2) was performed in order to identify chemical changes of bitumen after ageing. The binder sample, previously subjected to the RTFOT test, oxidized in the weathering chamber up to 100 hours of testing, considering the oxygen/carbon ratio as a parameter of oxidation process evaluation. The content of oxygen and the O/C ratio did not change after 100 hours of weathering ageing, indicating that the oxygen incorporating in bitumen did not occur after 100 and 150 hours of the weathering test. The oxygen content increases up to 100 hours of testing, and the carbonyl index increases from 0.06 to up 0.14 in the first 100 hours of ageing. The increase in oxygen content coincided with the increase in carbonyl index. After 100 hours of ageing, the oxygen content remained constant, as well as the carbonyl index, which maintains the value of 0.14. Exceptions to this trend are the carbonyl peaks that occurred after 40 hours and 150 hours of testing. One hypothesis that could explain the occurrence of these peaks would be the scissions of molecules in a given time, catalyzed by radiation, generating a great number of fragments and a temporary rise of carbonyl groups at the molecule ends, increasing the polarity and reactivity of the bitumen. Next, the fragments can be condensed, generating carbon-carbon bonds, reducing the energy state of the binder, and the carbonyl index decreases.

Asphalt binder samples submitted only to the RTFOT ageing (CAP0h) and after 150h of ageing (CAP150h) were submitted to TGA-MS analyses. Fig. 2 shows the decomposition profile of these two different materials under inert atmosphere at temperatures up to 800°C. The sample decomposition before ageing and after 150 hours of weathering ageing show similar profiles, characterized by a

Table 2. Elemental Analysis of Asphalt Binder Aged at Different Times in the Weathering Chamber and O/C Ratio for each Sample.

Conventional Binder	Carbon (C) Mass (%)	Hydrogen (H) Mass (%)	Nitrogen (N) Mass (%)	Oxygen (O) Mass (%)	O/C Ratio	H/C Ratio
Without Ageing	86.3	11.6	1.0	1.1	0.0096	1.6130
Aged for 50h	85.7	11.4	1.0	1.9	0.0166	1.5963
Aged for 100h	84.9	11.5	1.0	2.6	0.0230	1.6254
Aged for 150h	85.0	11.5	0.9	2.6	0.0230	1.6235

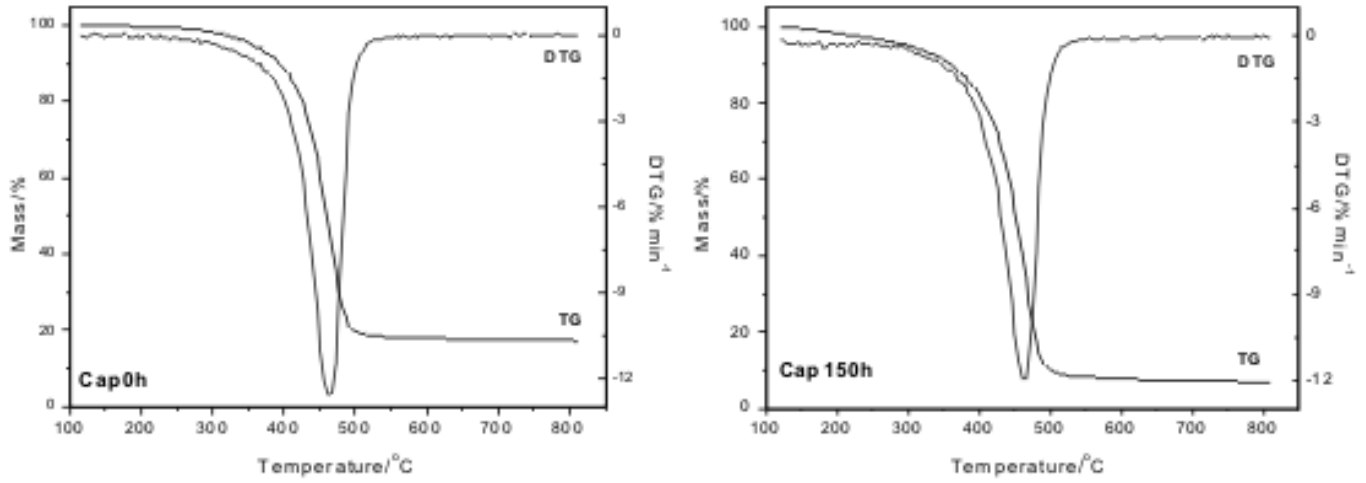

Fig. 2. Thermal Analysis of Asphalt Binder Without Ageing (Cap0h) and Asphalt Binder Aged for 150h (Cap150h). TGA and DTGA Curves Recorded in the TGA-MS Measurement.

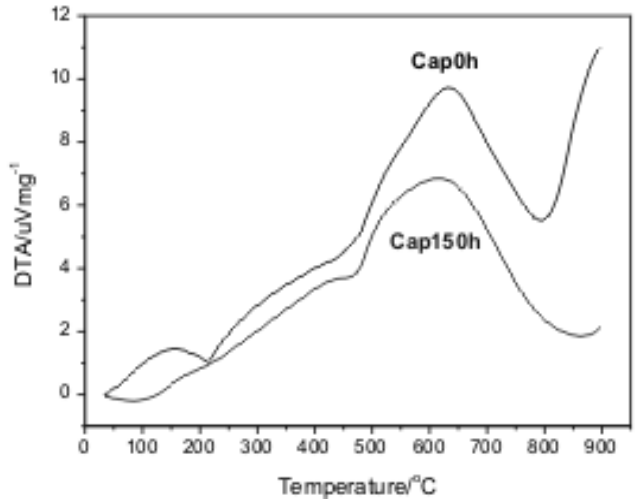

Fig. 3. DTA of Asphalt Binder without Ageing (Cap0h) and Asphalt Binder Aged for 150h (Cap150h) Recorded in the TGA-MS Measurement.

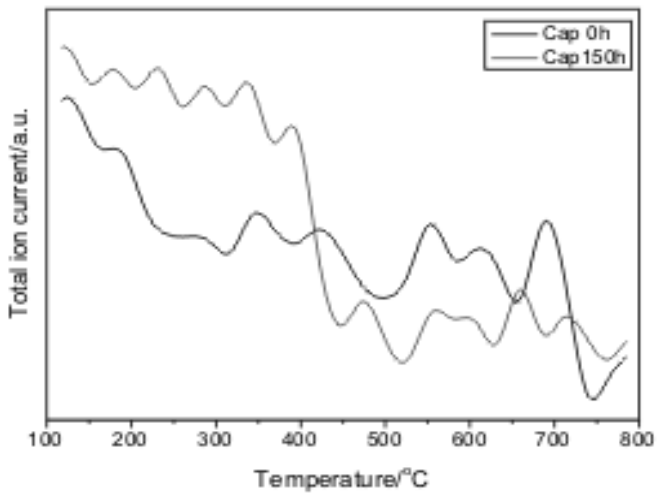

Fig. 4. Total Ion Current (TIC) Curves of the Evolved Gas Phase in the TGA-MS Analyses of Binder Samples Unaged and Aged for 150 Hours.

unique and intense mass loss at the temperature range 350°C-550°C. However, the amount of residue at the end of decomposition was 17% mass and 6% mass for the samples with RTFOT ageing and the binder samples aged for 150h in the weathering chamber, respectively. The more oxidized sample had higher oxygen content, and produced a higher content of CO and CO_2 compounds, and a lower amount of residue. A gasification process occurred to a greater extent in the sample aged for 150 hours. Although thermogravimetric curve for the binder sample aged for 150 hours shows a higher mass loss, DTGA results indicated that the decomposition kinetics is faster for binder sample without weathering ageing than for the binder sample aged for 150 hours. A sample with a higher degree of oxidation and cross linking, and with a more polymerized structure, tends to oxidize at a lower rate than a binder with a lower degree of oxidation. These results are in accordance with the hypothesis that a cyclization process of binder molecules can occur at 50 hours of weathering, after the peak observed at 40 hours of ageing, when scissions in molecules may have occurred.

Fig. 3 shows an overlay of the curves of Differential Thermal Analysis (DTA) for the two samples studied. The binders showed an exothermic event in the temperature range from 400 to 600℃ due to the sample degradation, confirming the results of TGA and DTGA. The binder sample without weathering ageing released a larger amount of heat during their degradation than the sample aged for 150 hours. The sample aged for 150h was less exothermic because the ageing changed its structure. Once the aged binder was more oxidized and cyclized, the degradation was not so effective releasing a lower amount of heat compared to the binder sample before the weathering ageing. A higher energy is necessary to break a higher number of chemical bonds present in the structure of aged binder sample, which released a lower amount of heat.

The mass spectrometric analysis of the released species (TGA-MS measurement) gave the total ion current (TIC) curves of binder samples without weathering ageing (Cap0h) and aged for 150 hours (Cap150h) as shown in Fig. 4. The two samples showed different patterns of TIC, suggesting that their decomposition products are different and/or these products have different arrangements inside the materials. The binder sample before weathering ageing showed a continuous TIC profile. The total ion current curve decreased as the temperature increased. However, the sample aged for 150 hours in the weathering chamber showed two distinct behaviors: (i) at temperatures lower than 400°C and (ii) at temperatures higher than 400°C. It is important to emphasize that the decomposition (mass loss) occurs at the temperature as the TIC pattern is modified for the aged sample. The decrease on the amount of evolved gases after decomposition is related to the fact that the sample aged for 150 hours has a lower fraction of smaller hydrocarbon fragments in its composition, which are more volatile, as shown in Table 3.

Table 3. Relative Intensities for Hydrocarbon Fragments Released of RTFOT Aged Samples (Cap0h) and the Binder Samples Aged for 150 Hours in the Weathering Chamber (Cap150h).

Fragment	m/z	Cap0h/%*	Cap150h/%*
CH_3^+	15	81.82	54.55
$C_2H_3^+$	27	42.42	39.39
$C_3H_5^+$	41	60.61	63.64
$C_3H_7^+$	43	45.45	27.27
$C_4H_7^+$	55	12.12	12.12
C_4H_8	56	15.15	9.09
C_5H_{10}	70	3.03	6.06
$C_7H_7^+$	91	0	3.03

*Relative intensity considering the purge signal (Argon) as 100%

To study the hydrocarbon fraction of the asphalt binder by TGA-MS, some fragments were selected. It is well known that hydrocarbons release some characteristic fragments, such as CH_3^+, $C_2H_3^+$, $C_3H_5^+$, $C_3H_7^+$, $C_4H_7^+$, C_4H_8, C_5H_{10} and $C_7H_7^+$ [5]. Table 3 shows the m/z ratio which correspond to these fragments and their relative intensity in the two analyzed samples obtained by TGA-MS. Bitumen appears aliphatic (high-intensity aliphatic fragments in the homologous series 15-27-41-43-55-56-70-91 m/z) and light [14]. Aliphatic molecules and fragments dominate the mass profile as reported in literature [14]. The sample of asphalt binder before

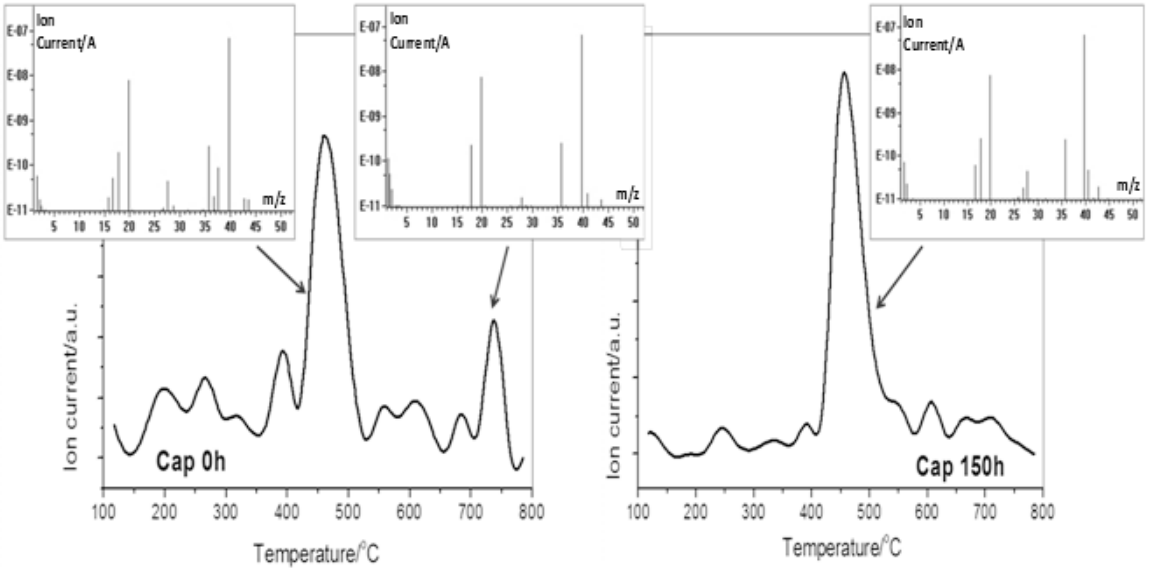

Fig. 5. Ion Current Curves of the Evolved Hydrocarbon Gases in the TGA-MS Analysis of the Unaged Samples and Aged for 150 Hours. In the Insets Mass Spectra Recorded Corresponding to Selected Decomposition Temperatures.

weathering ageing releases a higher fraction of lighter hydrocarbon fragments than the samples aged for 150h. The results of Table 3 agree with the suggestion that the size of hydrocarbon molecules present in asphalt composition increase with the ageing process.

The selected hydrocarbon fragments (Table 3) were grouped and the ion current generated by this group was compared between samples. Fig. 5 reports the spectra of gas decomposition products associated to the temperatures for samples before weathering ageing (Cap0h) and aged for 150 hours in the weathering chamber (Cap150h), obtained by TGA-MS.

The most important peak of hydrocarbon fragments matches with the DTGA minimum at around 460°C (as shown in Fig. 4). However, significant differences can be observed concerning the behavior at other temperatures. The sample before weathering ageing released hydrocarbon fragments all over the heating, especially at 200, 270, 390 and 740°C. The binder sample before weathering ageing had a lower degree of oxidation, a higher fraction of small molecules of different sizes and released hydrocarbon fragments of different sizes in a greater temperature range (200 a 740°C). The molecular weight distribution of the degradation product of an unaged bitumen sample is wider than the weight distribution of the degradation product of the aged sample.

Hydrogen and some oxidized molecules were also analyzed by TGA-MS in asphalt binder before weathering ageing and aged for 150 hours. The m/z ratio which corresponds to the analyzed fragments and their relative intensity are shown in Table 4.

The binder samples before weathering ageing released twice the hydrogen content than the samples aged for 150 hours. This result suggests that the weathering ageing process dehydrogenate the molecules. In other words, the binder becomes more oxidized or aromatized. The decrease of hydrogen/carbon ration (Table 2) at 50 hours of weathering ageing confirms this result. The more oxidized sample (Cap150h) released a higher content of all oxidized fragments such as CO, CO_2, CH_3O^+ and $CH_3CH_2O^+$. The

Table 4. Relative Intensities for H_2 and Oxidized Fragments Released of Samples Before Weathering Ageing (Cap0h) and Aged for 150 Hours (Cap150h)

Fragment	m/z	Cap0h/%*	Cap150h/%*
H_2	2	63.64	33.33
H_2O	18	99.09	99.09
CO	28	84.85	90.91
CH_3O^+	31	0	6.06
CO_2	44	62.73	63.64
$CH_3CH_2O^+$	45	3.03	21.21

*Relative intensity considering the purge signal (Argon) as 100%

functionalities formed in oxidation process should introduce an increase in the overall polarity of the bitumen [5], as seen in Table 4, which in turn will influence bitumen rheology, increasing the complex modulus.

FTIR spectroscopy results indicated that the asphalt binder showed a maximum value of carbonyl index at 150 hours and then a decrease of carbonyl index occurred. As ageing proceeds, ether bonds can be formed and the content of carbonyl groups decreases. Dehydrogenation occurs at 50 hours of weathering ageing and the oxygen/carbon ratio does not increase after 100 hours of ageing. The dehydrogenation can be related to the association or aromatization of the molecular fragments after the peak of carbonyl index at 40 hours of ageing. The sample aged for 150 hours showed a lower residue and a slower kinetics of mass loss than the binder sample before weathering ageing according to the TGA-MS results. All binders showed an exothermic event in the temperature range from 400 to 600℃ due to the sample degradation, but the sample aged for 150h was less exothermic according to the DTA results. The results of TGA-MS (Table 3) indicate that the size of hydrocarbon molecules present in asphalt composition increase with the ageing process. Many factors contributed to the loss of cohesive

properties of binder samples aged after 150 hours in the weathering chamber such as the increase of hydrocarbon molecular size, the occurrence of cyclization, cross linking, and formation of ether bonds. The interaction between molecules tends to be weaker as the size of the molecules increases.

Conclusions

The binder sample previously subjected to the RTFOT test oxidized in the weathering chamber up to 100 hours of testing, considering the oxygen/carbon ratio as a parameter of oxidation evaluation.

The hydrogen/carbon ratio decreased after 50 hours in the weathering chamber, indicating that a molecular reorganization occurred.

The decomposition of samples before weathering ageing and after 150 hours of weathering ageing show similar profiles of TGA-MS curve, characterized by a unique and intense mass loss at the temperature range 350^{o}C-550^{o}C. However, the amount of residue at the end of decomposition was 17% mass and 6% mass for the samples with RTFOT ageing and the binder samples aged for 150h in the weathering chamber, respectively.

The results of TGA-MS indicate that the size of hydrocarbon molecules present in asphalt composition increases with the ageing process.

The two samples showed different patterns of Total Ion Current (TIC) curves. The Total Ion Current curve of the sample before weathering ageing decreases continuously with the increase in temperature. However, the sample aged for 150 hours in the weathering chamber showed a sharp decrease of the Total Ion Current curve at 400^{o}C.

TGA-MS results indicated that the binder samples before the weathering ageing released twice the hydrogen content than the samples aged for 150 hours. The sample aged for 150 hours released a higher content of all oxidized fragments such as CO, CO_2, CH_3O^+ and $CH_3CH_2O^+$.

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