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Effects of different ageing methods on the chemical and rheological properties of bitumen

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Abstract: Bitumen undergoes ageing, which leads to changes in its chemical and rheological properties, thus becoming harder and more brittle in time. This study aims to compare the effects of different laboratory ageing methods on chemistry and rheology of three bitumen types, i.e. a Pen 40/60, a Pen 70/100 and a polymer modified bitumen (PmB). Four ageing protocols were applied: ageing at room temperature, oven ageing, the Pressure Ageing Vessel (PAV), and the Rolling Thin Film Oven Test (RTFOT) combined with PAV ageing. The effects of temperature, pressure, and ageing time were studied using dynamic shear tests and infrared spectroscopy. The results highlight the relationship between chemistry and rheology of bitumen. Bitumen hardening, which was revealed by an increase in complex modulus and a decrease in phase angle, was reflected in the growth of specific chemical functional groups. Among all materials, soft bitumen showed the greater tendency to oxidize. Different behaviour was observed for PmB that presented the highest resistance against oxidation among the studied bitumens, even though the reaction with oxygen caused the deterioration of the added polymer modifiers.

Author keywords: Bitumen; Ageing; Chemistry; Rheology; FTIR

Introduction

Numerous studies have investigated the sensitivity of asphalt mixtures to the damaging effects of climatic conditions and traffic loading. Especially, the ageing processes that occur during the service life of asphalt pavements lead to obtain mixtures that are more brittle in time and therefore, prone to ravelling and cracking (Molenaar et al. 2010). Various ageing mechanisms are identified in literature, namely physical hardening, loss of volatile components and oxidation. Among all, oxidation is considered to be the most important ageing process that can alter the chemical and rheological properties of bitumen.

The complex mechanical response of pavements is governed by the properties of asphalt mastics (Dondi et al. 2014) and essentially, it depends on the filler properties and on the way they interact with bitumen (Sangiorgi et al. 2016; Vignali et al. 2014; Mazzotta et al. 2016). However, bitumen is an organic material, as it mainly consists of carbon and hydrogen atoms (Lesueur 2009), which reacts with the oxygen present in the atmosphere and undergoes ageing. Actually, it is the ageing susceptibility of bitumen that leads to pavement damage (Lopes et al. 2012).

Oxidative ageing is a diffusion-driven phenomenon, which occurs due to photo-oxidation and thermal reaction between bitumen components and atmospheric oxygen (Lu et al. 2008). Oxygen diffuses into bitumen, changes the chemical features of bitumen and consequently, affects its physical properties. In general, the diffusion phenomenon is driven by the internal heat energy and is influenced by several parameters. The average radius of the diffusing molecules and the viscosity of the diffusion medium affect the rate of oxygen diffusion. Furthermore, intermolecular interactions, polarity and temperature influence indirectly this phenomenon (Karlsson and Isacsson 2003; Herrington 2012). Also, the temporal changes in the concentrations of oxygen and reactive bitumen species during the ageing reaction can affect the reaction itself (Herrington 2012).

Corbett (1969), as reported in Lesueur (2009), separated bitumen in four fractions: saturates aromatics, resins and asphaltenes. Each fraction is a continuum of molecules with different size, polarity and aromaticity. Redelius and Soenen (2015) reported that the largest size of bitumen macromolecules is defined by the crude oil source, while its smallest size is determined by the refinery process. Polar molecules influence the elastic behaviour of material by creating a network. On the contrary, non-polar fractions contribute to the viscous response of bitumen (Lerfald 2000). The reaction of bitumen and atmospheric oxygen leads to the growth of polar and aromatic molecules, which are able to reduce the mobility of molecules to flow; hence bitumen undergoes hardening and embrittlement.

In literature, several studies investigated the changes of bitumen fractions when subjected to ageing. It has been found that aromatics generate resin fractions, which in turn generate asphaltenes. On the other hand, the concentration of saturates changes slightly due to their low chemical reactivity (Lesueur 2009). The oxidation of bitumen fractions generates a number of functional groups such as ketones, sulfoxides, dicarboxylic anhydrides, and carboxylic acids. Ketones are formed from specific aromatic molecules, which have two adjacent benzylic carbon moieties. When those molecules are oxidized, first, they result in the formation of dicarboxylic anhydride and then, ketones are made by condensation. Carboxylic acids are produced in small amounts. On the other hand, sulfoxides are the result of organic sulphides oxidation, which represent functional moieties of many types of asphalt (Petersen 2009).

The types of oxidation products are consistently the same for bitumen from different sources, but their amount may differ especially between unmodified and polymer modified bitumen (Lu et al. 2008). In reality, the concentration of each product and their tendency to oxidize are influenced by crude oil origin. As sulphides are more reactive, sulfoxides have higher production rate and are formed faster than ketones. After that, ketones are formed, which finally yield anhydrides and carboxylic acids. Lesueur (2009) stated that sulfoxides are thermally unstable and they reach a constant level, which depends on initial sulphur content and oxygen diffusion into the material. In contrast, ketones and carboxylic acids are more stable, but they do not always reach an asymptotic value. Also, Lesueur (2009) indicated that field aged bitumen usually achieves a constant value, while an asymptotic value is not reached when bitumen is laboratory aged. On the other hand, Liu et al. (1996) showed that the rate of carbonyl formation becomes constant for all laboratory aged bitumen after an initial higher rate period. More recently, Lu et al. (2008) confirmed the increase of carbonyls and sulfoxides molecules after standard short- and long-term ageing protocols, namely after Rolling Thin Film Oven Test (RTFOT) and Pressure Ageing Vessel (PAV) ageing. They compared the formation of these functional groups for unmodified and Styrene-Butadiene-Styrene (SBS) modified bitumen through infrared spectroscopy. Sulfoxides were observed to grow more in the neat standard bitumen.

Conversely, a greater presence of carbonyl was found for the modified material. The researchers attributed this increase to both oxidation and degradation of polymers.

The rheological and physical characteristics of bitumen are strongly related to the chemical ones. Ageing causes stiffening of the bitumen as shown by an increase of complex modulus and a decrease of phase angle (Lu et al. 2008; Molenaar et al. 2010). Moreover, oxidation increases bitumen viscosity, which depends on the type and strength of molecular interactions. Petersen (2009) reported that bitumens with high content of metals, especially vanadium, show major sensitivity to viscosity. In addition, the values of softening point and penetration grade change after oxidation. Lu et al. (2008) reported that the softening point increases for natural bitumen, while the opposite trend was found for polymer modified materials. On the contrary, the penetration value decreases with increasing ageing time.

Research objectives

This study aims to compare the effects of different laboratory ageing methods on the chemistry and rheology of bitumen. The influence of temperature, pressure, and ageing time were studied using the Dynamic Shear Rheometer (DSR) tests and Fourier Transform Infrared Spectroscopy (FTIR). Also, the properties of aged bitumens were compared with those of the unaged fresh materials to study the susceptibility of the different bitumen types to ageing.

Experimental research

To study the effects of different laboratory ageing methods on bitumen chemistry and rheology four ageing protocols were applied: ageing at room temperature, oven ageing, Pressure Ageing Vessel (PAV) and Rolling Thin Film Oven Test (RTFOT) combined with PAV ageing. The effects of temperature, pressure, and ageing time on three bitumens types were studied by means of DSR and FTIR tests. Two replicate samples of each bitumen type were tested at every ageing condition to determine statistically reliable results. In all the cases analysed, similar results were obtained.

Materials and sample preparation

Three bitumen types were adopted throughout this study, two standard or neat bitumens and one polymer modified bitumen. The standard materials varied with respect to their penetration grade; a Q8 Pen 40/60 bitumen and a Q8 Pen 70/100 bitumen were used. The Q8 polymer modified bitumen with a grade QmB 45/80 - 65 was obtained by the addition of Styrene-Butadiene-Styrene (SBS) polymers, which are often used to enhance the durability and resistance of bitumen (Dondi et al. 2016). Table 1 lists the properties of the materials.

Cylindrical bitumen samples were prepared according to the European Standard NEN-EN 12594:2014. The diameter of the samples was equal to 27.50 mm and their thickness was 2 mm. Bitumen, in quantity lower than one liter, was heated in the oven for 120 minutes at temperature that did not exceed the softening point of each specific bitumen type more than 100°C. The liquid bitumen was stirred and poured in a silicon mould to cool down. Then, the mould was placed in a refrigerator for about 15 minutes. The samples were finally demoulded and were ready for ageing in the lab.

Ageing methods

Four ageing methods were applied, namely ageing at room temperature, oven ageing, ageing by means of the Pressure Ageing Vessel, and an ageing protocol that included the combination of Rolling Thin Film Oven Test and PAV ageing.

Ageing at room temperature was performed at five different time intervals of 5, 10, 15, 20 and 25 days. The average room temperature was 24.6°C. During room ageing the samples were not homogenized, as this would require the application of heat that could affect the results. Oven ageing was carried out at 135°C for 60 hours, and 5, 10, 15 days. A standard quantity of bitumen (90±3 g) was heated and poured into aluminium containers forming a 1 cm thick layer. During ageing, bitumen was manually stirred, rotating the trays clockwise and counter-clockwise once a day in order to encourage the homogeneous ageing of the samples. The Pressure Ageing Vessel test was performed at standard conditions, i.e. ageing at 100°C temperature and 2.1 MPa pressure for 20 hours, following the NEN-EN 14769:2005 European Standard. Moreover, PAV test was realized at the same temperature and pressure but for a double ageing time (40 hours). Finally, the short- and long-term standard ageing procedures were combined; first the samples were aged using the RTFOT according to the NEN-EN 12607-1:2014 European Standard followed by PAV at standard conditions. The aforementioned ageing methods are listed in Table 2.

Test methods

The effects of ageing were evaluated by means Dynamic Shear Rheometer tests and Fourier Transform Infrared Spectrometry. The Perkin Elmer Spectrum 100 FTIR spectrometer was used in the Attenuated Total Reflectance (ATR) mode to identify the chemical functional groups of the bitumens. The wavelength of the reflected beam is characteristic of each element and indicates the presence of specific functional groups. Using the ATR technique, sample preparation was simple. A small sample of material was taken using a spatula and placed under the FTIR anvil. The FTIR spectrum was obtained in the spectral range between 4,000 and 600 cm^{-1} with a scanning resolution of 4 cm^{-1} averaging five scans for each measurement in order to increase the signal-to-noise ratio of the measurements. Then the spectrum was normalized to allow the quantitative analysis of the results.

The oxidation of bitumen was evaluated at specific bands of wavelengths, which can reveal the formation of the characteristic oxidation products. Researchers have identified four specific wavelengths where the changes due to ageing can be observed. Due to the complexity of the chemical composition of bitumen a fixed peak cannot be found for bitumens especially if the origin of materials is different (Van der Bergh 2011). For this reason, in this study, the effects of ageing were analyzed considering specific bands of wavelength, as defined by Lamontagne et al (2001), and the corresponding area under those bands (Van der Bergh 2011). The peak areas were evaluated using semi-quantitative analysis and then the four ageing indices, namely the aromaticity, long chain, carbonyl and sulfoxide were determined, as presented in Table 3.

Bitumen rheology was characterized through DSR tests. The Anton Paar EC-Twist 502 device was used to analyse the material response over a wide range of temperatures and frequencies that occur during the pavement service conditions. First, the Linear Viscoelastic Range (LVE) of each bitumen type was determined by means of amplitude sweep tests. The maximum strain value within the linear viscoelastic range was 0.9% for Pen 40/60, 1.4% for Pen 70/100 and 1.0% for PmB. These values were chosen to be the strain amplitude values applied during the frequency sweep tests for each bitumen. The tests were performed using the parallel plate configuration in a strain controlled mode, applying an oscillatory shear stress on a sample of 1 mm thickness. The tests were performed at a range of frequencies from 10 Hz to 0.1 Hz and at five temperatures, specifically at 10°C, 20°C, 30°C, 40°C and 50°C.

Results and discussion

Fourier Transform Infrared Spectroscopy analysis

The FTIR spectra were obtained in a wavelength range from 4,000 to 600 cm^{-1}. However, the changes due to ageing can be found at wavelengths less than 1800 cm^{-1}, as shown in Fig. 1.

Fig. 2 shows the aromaticity and long chain indices for all bitumen types after the application of the various ageing methods. The aromaticity index denotes the aromatization of bitumen and relates to the increase of viscosity (Nivitha et al. 2016). The results show that the aromaticity index does not vary significantly after ageing at room temperature for none of the three bitumen types. In contrast, oven ageing seems to affect the aromatic fraction. The value of the aromaticity index increases in time for the polymer modified bitumen, especially after five days of oven ageing. For the neat bitumens, the aromatic fraction shows an increase after five days of oven ageing similar to the PmB, but then remains relatively constant. The standard PAV method does not influence significantly the value of the aromaticity index compared to its value before ageing. The application of the extended PAV protocol results in an increase of the aromaticity index similar to this of prolonged oven ageing.

Nivitha et al. (2016) observed a decrease of the long chain index with increasing ageing time. Similarly, Fig. 2 shows that the long chain index decreases with extended oven ageing for all bitumens. Depending on the bitumen type, the index seems to decrease with ageing time (for PmB and Pen 70/100) or reaches a steady state after five days of oven ageing (Pen 40/60). The evolution of the long chain index does not show a specific trend with time when aged at room temperature.

On the contrary, Fig. 3 shows that the values of the carbonyl and sulfoxide indices increase during ageing; the extent of increase depends on the ageing method applied to the bitumen samples. The carbonyl index denotes the formation of ketones, dicarboxylic anhydrides and carboxylic acids due to the reaction between carbon and oxygen (C=O), whereas the sulfoxide index denotes the S=O stretching due to the oxidation of sulphides. Both indices are identified as key parameters when studying bitumen ageing, as the carbonyl groups and sulfoxides are the most important oxidation products.

It is interesting to note that the carbonyl index has zero value after room ageing, regardless of the duration of ageing and the bitumen type. On the other hand, ageing in the oven at 135°C causes an increase of the carbonyl index. The duration of oven ageing influenced the formation of carbonyl compounds, as indicated by the growth of the carbonyl index. After 60 hours of oven ageing, the carbonyl index of both neat bitumens remains zero. After 5 days of oven ageing, a slight increase is observed for the harder Pen 40/60 bitumen, whereas a higher value is obtained for the Pen 70/100. However, after 10 days of oven ageing the value of the carbonyl index increases substantially for both bitumen types and becomes one order of magnitude higher than its value at five days. Overall, the formation rate of carbonyl compounds is higher for Pen 70/100 as indicated by the absolute values of the carbonyl index, which are one order of magnitude higher than those of the harder bitumen. The formation of carbonyl compounds for the PmB occurs after 10 days of oven ageing, unlike for the unmodified bitumens. The delay in carbonyl formation can be attributed to the inherently low susceptibility of polymer modified bitumens to higher temperatures.

The production of sulfoxides does not follow the same trend. Sulfoxides are formed to some extent when the samples are aged at room temperature, indicating that the natural content of sulphur reacts with atmospheric oxygen even at lower temperatures. It is, therefore, shown that the sulfoxides (S=O) have a higher production rate than the carbonyls. This finding verifies the higher rate production of sulfoxides than ketones reported by Lesueur (2009).

Sulfoxides in Pen 70/100 bitumen are also formed at a higher rate compared to Pen 40/60 as indicated by the sulfoxide index. The value of the sulfoxide index for Pen 70/100 changed by 33%-40% after ageing at room temperature and 52-62% after oven ageing compared to its value at unaged conditions. In contrast, the sulfoxide index for Pen 40/60 increased only by 12% after room ageing and 11-16% after oven ageing compared to the reference unaged value. These findings indicate that the soft bitumen is more susceptible to oxidative ageing than the harder Pen 40/60 bitumen. For the unmodified bitumens, the application of the standard PAV method, combined or not with the standard RTFOT method, results in the growth of both the sulfoxide and carbonyl index. From a comparison between the O60h protocol and the PAVS protocol, it can be observed that the application of pressures higher than the atmospheric pressure promotes the formation of carbonyl compounds, even though the PAVS ageing was performed for less time and at lower temperature than O60h ageing after which no carbonyls were produced.

On the other hand, the sulfoxide index for the PmB did not vary considerably with ageing time at room temperature, whereas oven ageing caused an increase in its value after 5 days of ageing. The application of high temperature and pressure (PAVS, PAVM and RTFOT+PAVS ageing methods) affected the growth of sulfoxides, but did not increase significantly the amount of carbonyls when using the two standard ageing protocols. It was observed that the application of PAVS and RTFOT+PAVS ageing resulted in a minor increase of the carbonyl index for the PmB, while the extended PAVM protocol had a significant effect on the carbonyl index, possibly due to the prolonged ageing time. The presence of styrene and butadiene copolymers in the PmB is detected at 700 cm^{-1} and 968 cm^{-1} wavelength, respectively (BRRC 2013). The polymer peaks after the application of each ageing method are listed in Table 3. The results show that the styrene copolymer degrades with ageing, especially after oven ageing and the PAV ageing protocols.

Among the various ageing methods the PAVM and the prolonged oven ageing were the most effective ageing protocols, as indicated by the changes in the carbonyl and sulfoxide indices. Both the carbonyl and sulfoxide indices were found to increase during ageing. However, it has been observed that the formation of carbonyl compounds was mainly the result of applying high temperature. It is therefore suggested that the carbonyl index and the relative increase of the sulfoxide index (compared to a reference unaged value) are considered together when characterizing ageing in bituminous mixtures; especially in the case of bitumen recovered from asphalt pavements, where such high temperatures do not usually take place, using only the carbonyl index as ageing indicator may lead to incorrect conclusions with regard to the bitumen susceptibility to ageing. The graph in Fig. 4 compares the development of oxidation products after three ageing methods, namely after 25 days of room ageing, 15 days of oven ageing and the application of PAVM ageing. The formation of oxidation products varies with the ageing method for all bitumens. Nevertheless, the results confirm the greater sensitivity of Pen 70/100 bitumen to oxidize.

Dynamic shear rheometer test results

Oxidative ageing is known to alter the rheological properties of bitumens, causing an increase in complex modulus and a decrease in phase angle. Every bitumen type responds in a different way to ageing, and therefore the changes in physical properties can be different, mainly due to its dependency on oxidation kinetics (Juristyarini et al. 2011). Fig. 5 and Fig. 6 show the master curves of Pen 40/60 and Pen 70/100 bitumens, respectively, at unaged state and after the application of the R25d, O15d, RTFTO+PAVS and PAVM ageing protocols.

It can be observed that the most noticeable changes in complex modulus due to ageing were recorded at low frequencies as the bitumen was in the rubbery flow region, whereas minor changes were observed at high frequencies (glassy transition region). Similar to the results obtained from the FTIR measurements, it was observed that oven ageing, at 135°C for 15 days, affected the rheology of bitumens more than the combined effects of high temperature and pressure. Again, ageing at room temperature for 25 days did not result in significant differences with respect to the rheological response of fresh (unaged) bitumen. It seems that oxidation took place, but in a very slow rate, confirming that bitumen reacts slowly with atmospheric oxygen (Herrington 2012). The phase angle of the unmodified binders decreased considerably with ageing, indicating an increase in elasticity of bitumen and a reduction of its flow characteristics. Oven ageing, in particular, caused a great increase in phase angle especially at low frequencies (high temperatures), which in combination to the increase of complex modulus, is an indication of embrittlement of the material.

Fig. 7 shows the complex modulus and phase angle master curves for the PmB. The complex modulus of PmB increased with ageing, but to a less extent if compared to the unmodified bitumens. It was observed that after 15 days oven ageing the complex modulus, at low frequencies, increased by one order of magnitude. Overall, the rheological response of the PmB after oven ageing did not differ significantly with its response after the application of the PAVM and PAVS+RTFOT protocols, in contrast to what was observed for the unmodified binders. This possibly occurs due to the high temperature susceptibility of the polymer modified bitumen, which can undergo higher temperatures for prolonged ageing times.

The phase angle master curve at unaged condition shows a characteristic plateau in the intermediate frequency area. This feature actually shows the presence of polymer into the bitumen chemical structure. This characteristic plateau in the phase angle master curves is maintained after 25 days of room temperature ageing. However, the application of high temperature for prolonged time (O15d) or combinations of high temperature and pressure (PAVM and RTFOT+PAVS) caused a smoothening of the curve, as shown in Fig. 10. This result may be explained by the fact that degradation of the polymer modifier can occur after the specific ageing protocols. The FTIR measurements support this hypothesis as it was observed that the styrene copolymer peak degraded with ageing, especially after the application of the O15d and PAVM and RTFOT+PAVS protocols. In general, based on the rheological properties, the PmB was found to have greater resistance to the oxidation processes, while Pen 70/100 bitumen was highly sensitive to ageing.

Conclusions

This study aimed to compare the effects of different laboratory ageing methods on the chemical and rheological properties of unmodified and SBS modified bitumens. The evolution of the chemical properties during ageing was monitored using the indices that correspond to aromaticity and long chains, as well as to the formation of carbonyls and sulfoxides. Moreover, the characteristic peaks of the modifiers were considered. The changes in rheology were evaluated on the basis of complex modulus and phase angle master curves.

The influence of high temperature was clearly observed for unmodified bitumens when compared to the polymer modified bitumen in terms of both thermo-sensitivity reduction (Vignali et al. 2016) and ageing response. The ageing indexes and the rheological response of both neat bitumen types, Pen 40/60 and Pen 70/100, demonstrate that high temperatures applied for a prolonged time (≥10 days) influence more the bitumen response than the combined effects of high temperature and pressure due to PAV and RTFOT. For the polymer modified bitumen, though, oven ageing at high temperature did not result in large differences in its rheological response when compared to the response after the application of the PAVM and PAVS+RTFOT protocols, possibly due to the high temperature susceptibility of the polymer modified bitumen. Nevertheless, the characteristic plateau in the phase angle master curve at unaged condition, denoting the presence of polymer modifiers, was smoothened out after the application of high temperature for prolonged time or combinations of high temperature and pressure. It was hypothesized that the aforementioned ageing conditions degrade the polymer modifier; the evolution of the characteristic FTIR peaks of the modifiers confirmed this hypothesis.

The aromaticity index and the long chains index did not vary significantly after ageing at room temperatures; nevertheless, the application of high temperatures and pressure resulted in a decrease of the long chain index and an increase of the aromaticity index. In some cases, no specific trend was observed with respect to ageing time or temperature. In contrast, both the carbonyl and sulfoxide indices increased with ageing. Carbonyls formed at a slower rate than the sulfoxides. Ageing at room temperature did not stimulate carbonyl formation for any of the bitumens; the carbonyl index remained equal to zero. After 60 hrs of oven ageing at high temperature for the unmodified bitumens (or five days for the polymer modified bitumen) carbonyl compounds were formed, as indicated by the growth of the carbonyl index.

Similarly, ageing at room temperature did not influence the rheological properties of the bitumens. Overall, bitumen hardening, which was revealed by an increase in complex modulus and a decrease in phase angle, was reflected in the growth of specific chemical functional groups. The polymer modified bitumen showed a highest resistance against the oxidation, thus against stiffening and embrittlement, than neat standard bitumens. Among the unmodified bitumens, the soft Pen 70/100 bitumen exhibited the greater tendency to stiffen compared to the harder Pen 40/60 bitumen.

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Table 1. Bitumen Specifications

Property	Unit	Pen 40/60	Pen 70/100	PmB
Penetration @25°C	mm	40/60	70/100	45/80
Softening Point	ºC	49	44	65
Fraass Breaking Point	ºC	-7	-14	-15
Dynamic viscosity @60°C	Pa·s	175	160	-
Complex shear modulus 1.59Hz - @60°C	kPa	3.6	1.8	12
Phase angle 1.6Hz - @60°C	º	87	88	69

Table 2. Applied Ageing Methods

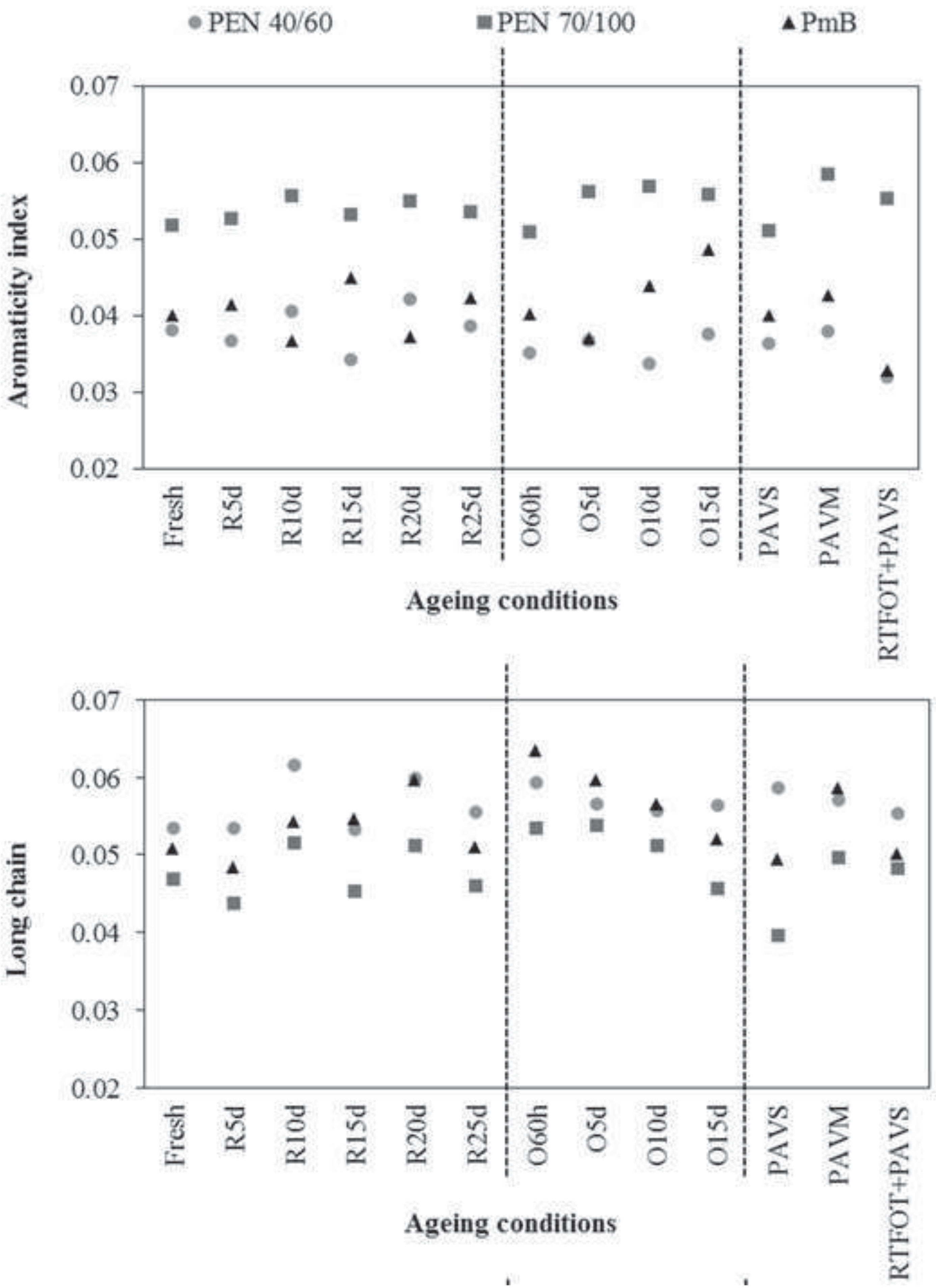
Ageing method	Ageing time	Abbreviation
Fresh (unaged)	-	F
Room @24.6^{o}C	5 days	R5d
	10 days	R10d
	15 days	R15d
	20 days	R20d
	25 days	R25d
Oven @135^{o}C	60 hours	O60h
	5 days	O5d
	10 days	O10d
	15 days	O15d
PAV @100^{o}C & 2.1MPa	20 hours	PAVS
	40 hours	PAVM
RTFOT+PAV	Standard conditions	RTFOT+PAVS

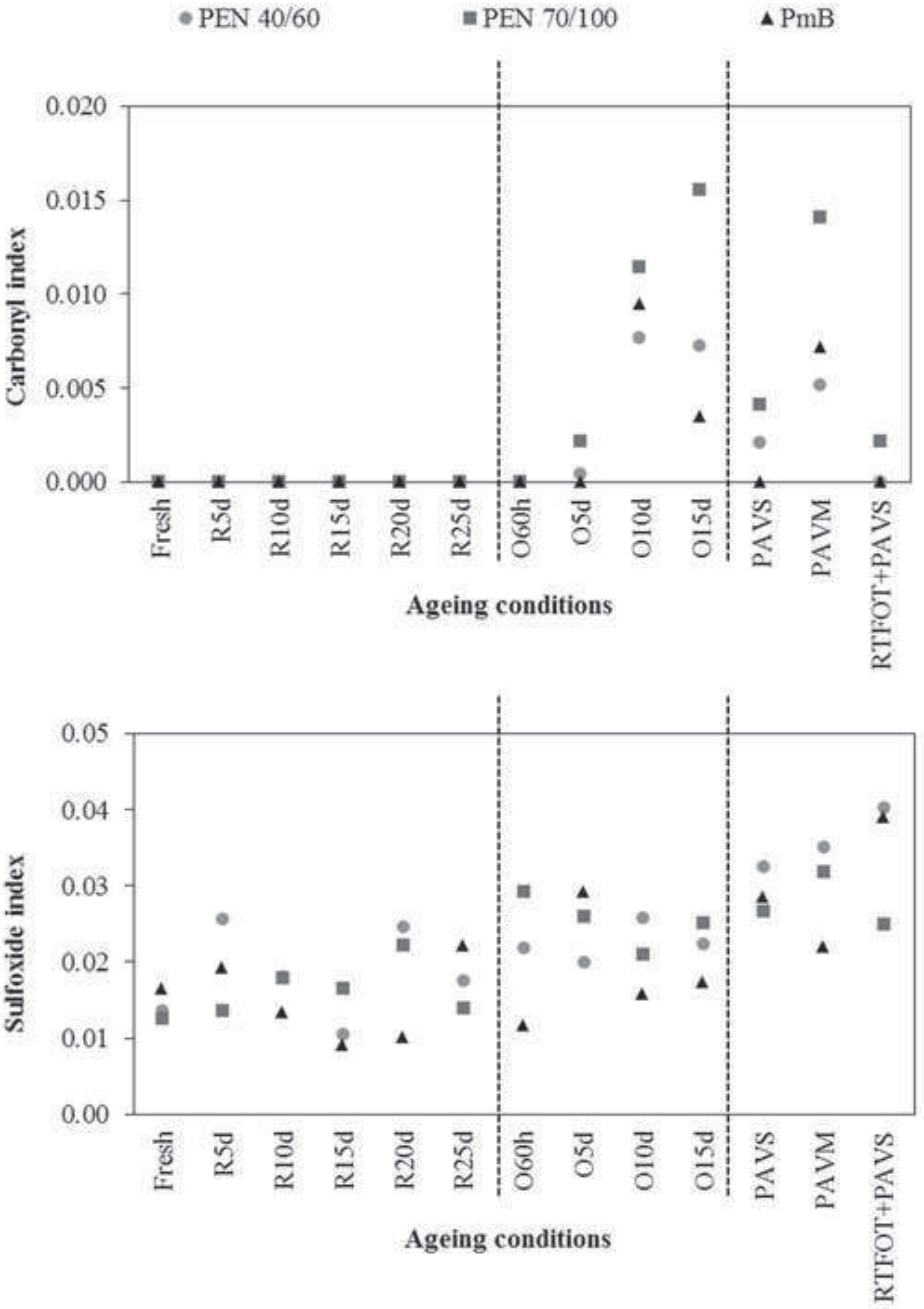
Table 3. Indices calculated for all bitumens

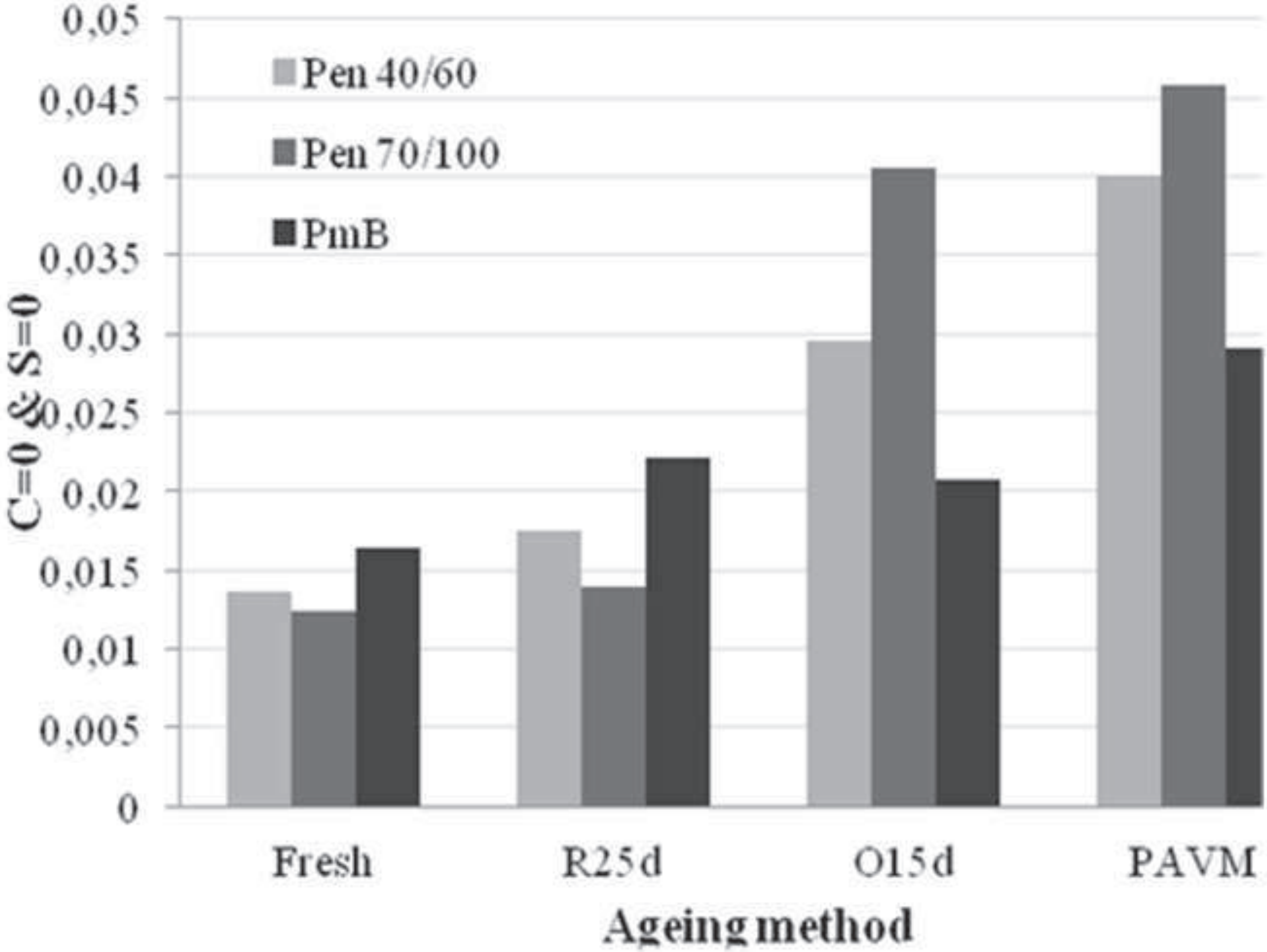
Aromaticity	$A_{1670-1535}/\sum A$
Long chain	$A_{734-710}/A_{1376}+A_{1460}$
Carbonyl	$A_{1753-1660}/\sum A$
Sulfoxide	$A_{1047-995}/\sum A$
$\sum A=A_{(2953,2862)}+A_{1700}+A_{1600}+A_{1460}+A_{1376}+A_{1030}+A_{864}+A_{814}+A_{743}+A_{724}$	

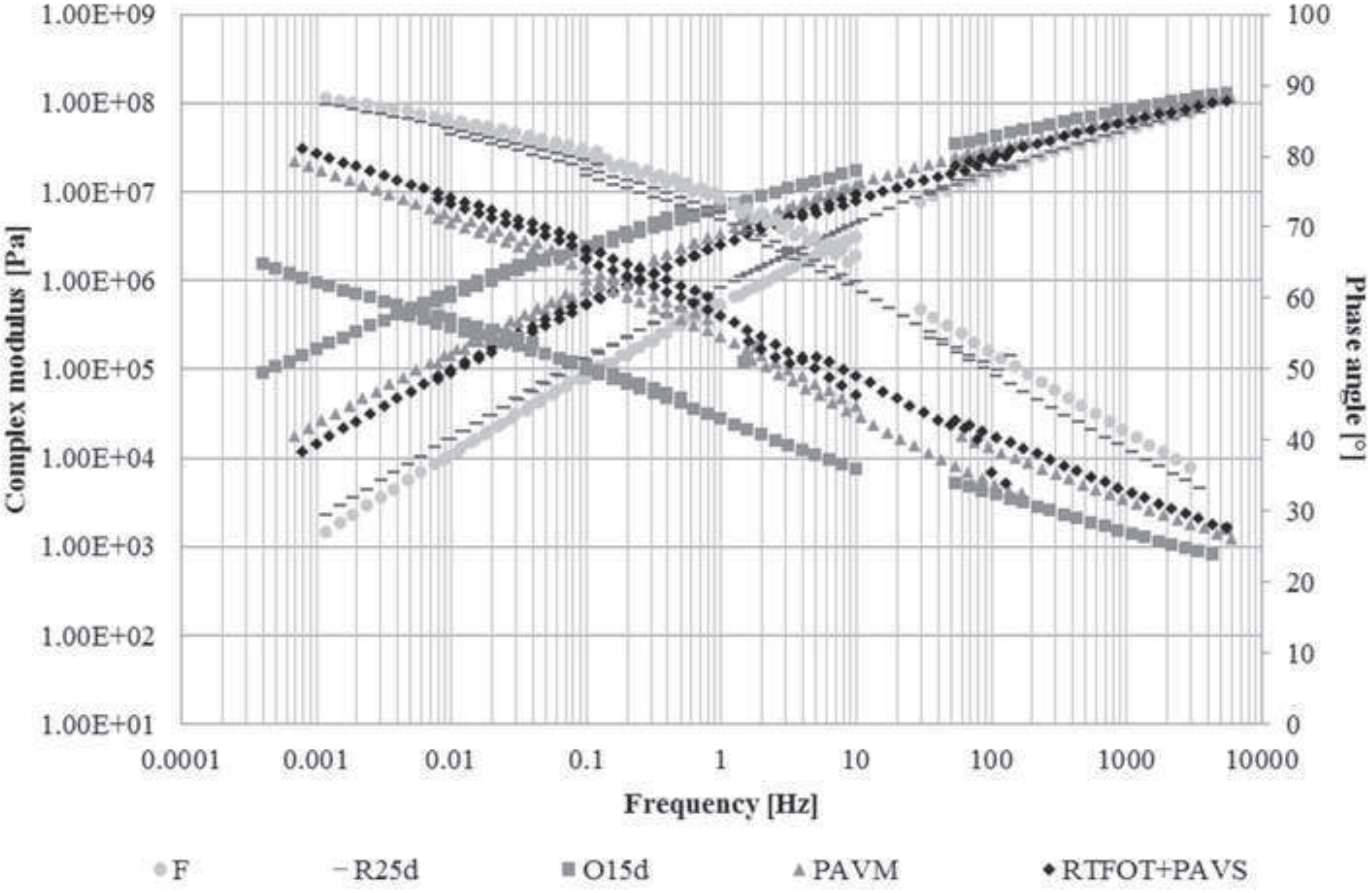
Table 4. Polymer Peaks of Polymer Modified Bitumen obtained by FTIR

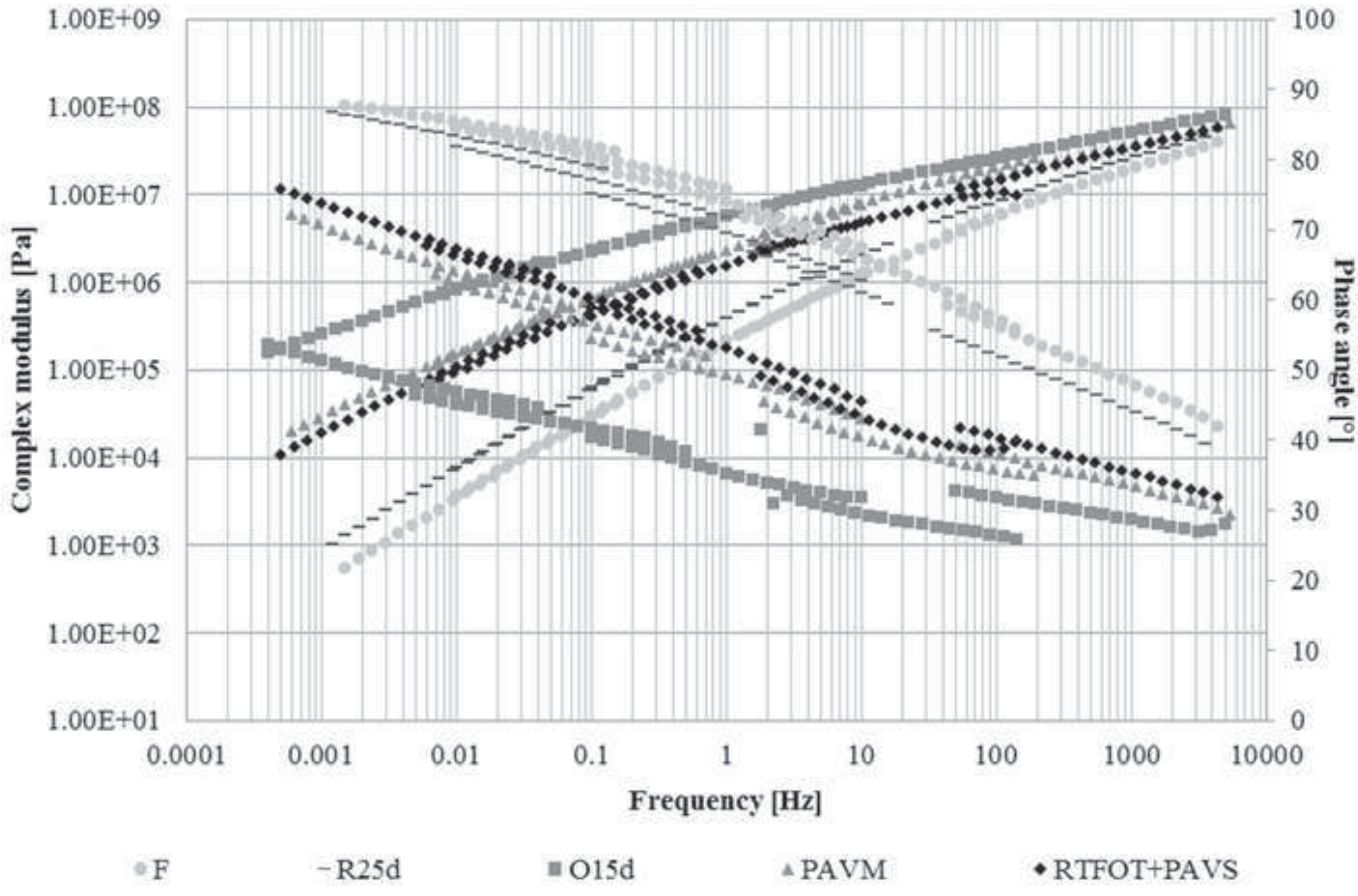
Ageing method	Styrene peak [700 cm-1]	Butadiene peak [968 cm-1]
fresh (unaged)	0.3436	0.2102
R5d	0.2995	0.1954
R10d	0.3069	0.2067
R15d	0.3001	0.1862
R20d	0.2726	0.1859
R25d	0.2877	0.1890
O60h	0.3219	0.2137
O5d	0.3156	0.2173
O10d	0.3006	0.2147
O15d	0.3085	0.2150
PAVS	0.3097	0.2179
PAVM	0.3036	0.2233
RTFOT+PAVS	0.3251	0.2334

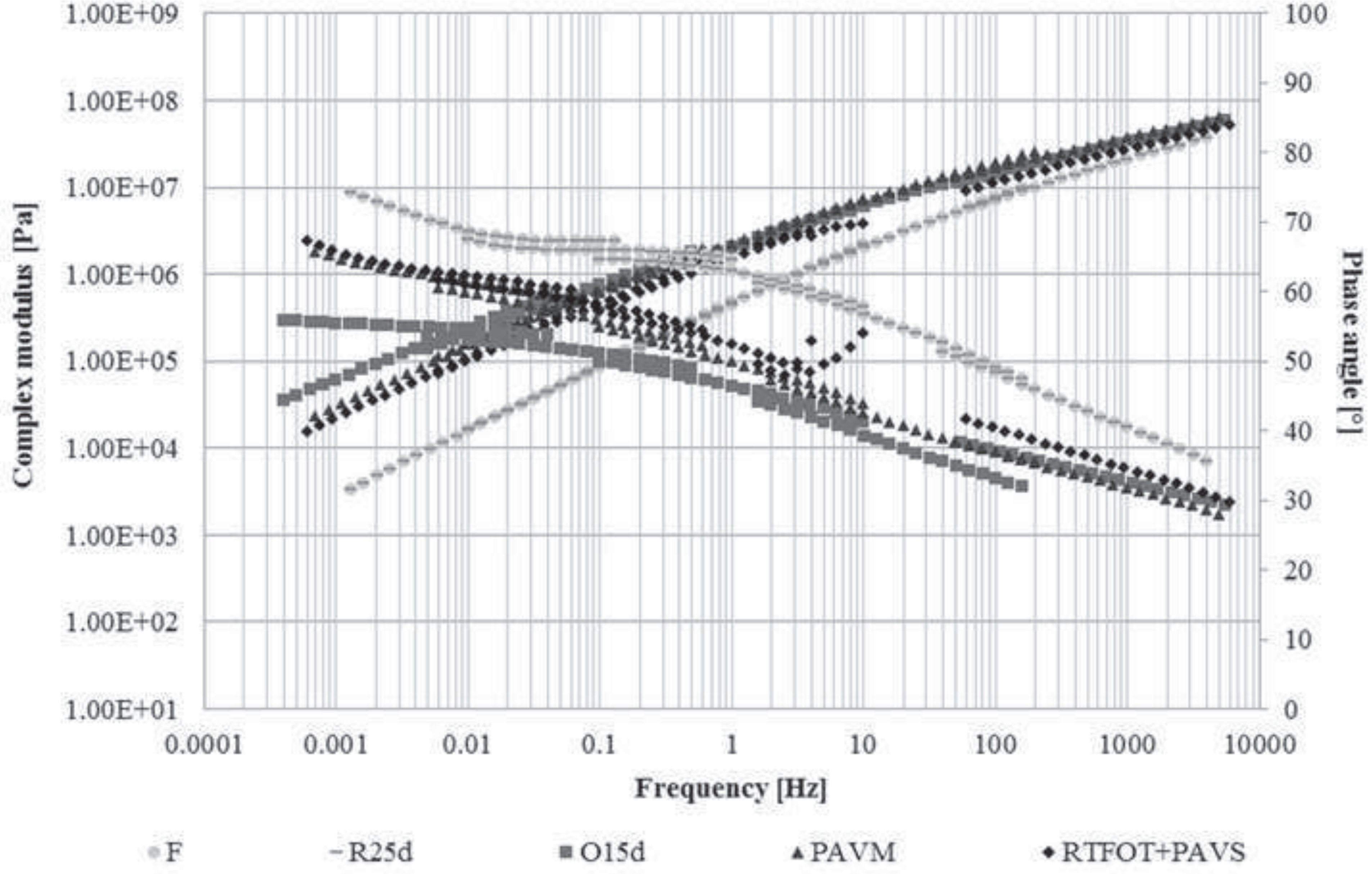

● PEN 40/60
■ PEN 70/100
▲ PmB
Aromaticity index
0.07
0.06
0.05
0.04
0.03
0.02
Fresh
R5d
R10d
R15d
R20d
R25d
O60h
O5d
O10d
O15d
PAVS
PAVM
RTFOT+PAVS
Ageing conditions
Long chain
0.07
0.06
0.05
0.04
0.03
0.02
Fresh
R5d
R10d
R15d
R20d
R25d
O60h
O5d
O10d
O15d
PAVS
PAVM
RTFOT+PAVS
Ageing conditions

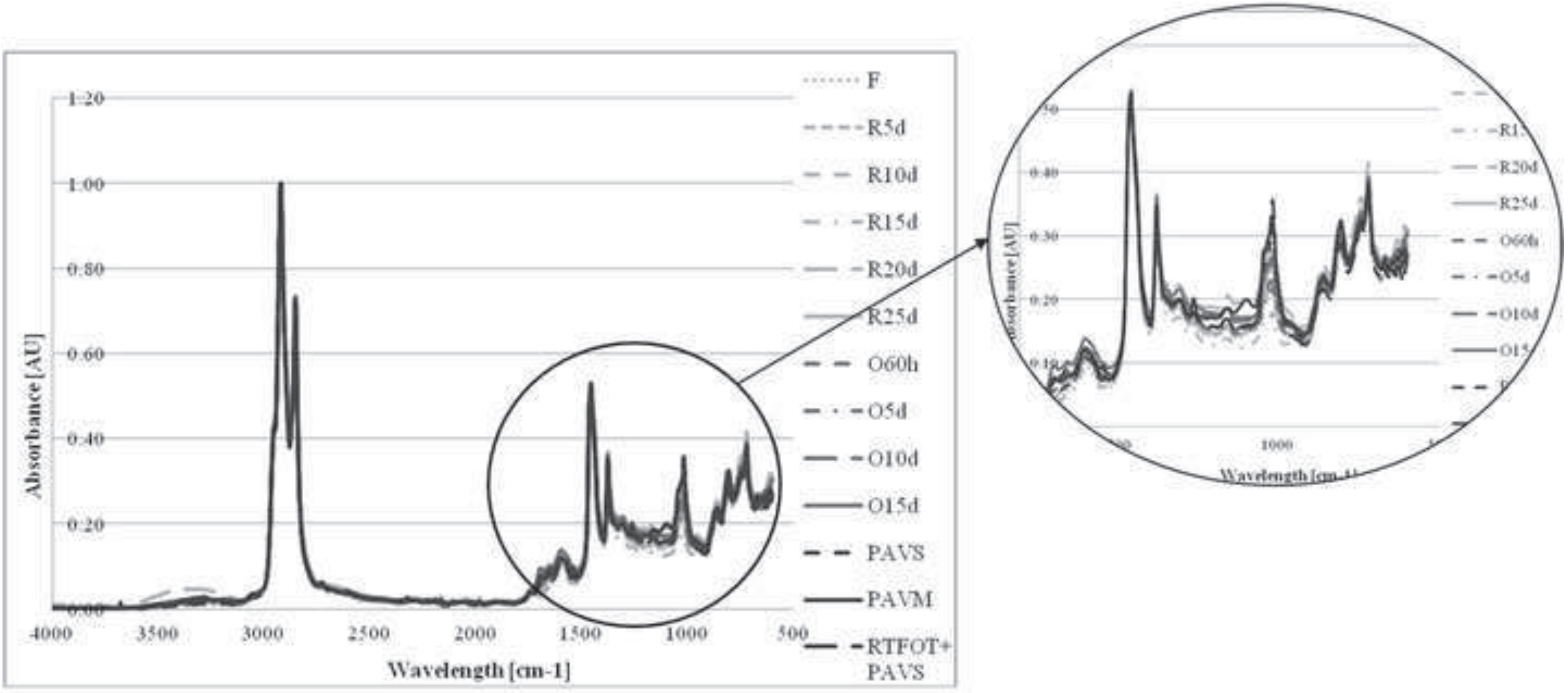

● PEN 40/60
■ PEN 70/100
▲ PmB
Carbonyl index
0.020
0.015
0.010
0.005
0.000
Fresh
R5d
R10d
R15d
R20d
R25d
O60h
O5d
O10d
O15d
PAVS
PAVM
RTFOT+PAVS
Ageing conditions
Sulfoxide index
0.05
0.04
0.03
0.02
0.01
0.00
Fresh
R5d
R10d
R15d
R20d
R25d
O60h
O5d
O10d
O15d
PAVS
PAVM
RTFOT+PAVS
Ageing conditions


0,05
0,045
0,04
0,035
0,03
0,025
0,02
0,015
0,01
0,005
0
C=0 & S=0
Pen 40/60
Pen 70/100
PmB
Fresh
R25d
O15d
PAVM
Ageing method


1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
Complex modulus [Pa]
100
90
80
70
60
50
40
30
20
10
0
Phase angle [°]
0.0001
0.001
0.01
0.1
1
10
100
1000
10000
Frequency [Hz]
● F
− R25d
■ O15d
▲ PAVM
◆ RTFOT+PAVS


Complex modulus [Pa]
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
Phase angle [°]
100
90
80
70
60
50
40
30
20
10
0
0.0001
0.001
0.01
0.1
1
10
100
1000
10000
Frequency [Hz]
● F
- R25d
■ O15d
▲ PAVM
◆ RTFOT+PAVS


1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
Complex modulus [Pa]
100
90
80
70
60
50
40
30
20
10
0
Phase angle [°]
0.0001
0.001
0.01
0.1
1
10
100
1000
10000
Frequency [Hz]
● F
− R25d
■ O15d
▲ PAVM
◆ RTFOT+PAVS


1.20
1.00
0.80
0.60
0.40
0.20
0.00
Absorbance [AU]
4000
3500
3000
2500
2000
1500
1000
500
Wavelength [cm-1]
F
R5d
R10d
R15d
R20d
R25d
O60h
O5d
O10d
O15d
PAVS
PAVM
RTFOT+ PAVS
0.40
0.30
0.20
0.10
Absorbance [AU]
1000
Wavelength [cm-1]
R20d
R25d
O60h
O5d
O10d

List of figure captions

Fig. 1. Detail of the FTIR spectra.

Fig. 2. Aromaticity and long chain indices for all bitumen types after the application of the different ageing methods.

Fig. 3. Carbonyl and sulfoxide indices for all bitumen types.

Fig. 4. Growth of C=O and S=O oxidation products of laboratory aged bitumens.

Fig. 5. Master curves of complex modulus and phase angle of Pen 40/60 at different ageing conditions.

Fig. 6. Master curves of complex modulus and phase angle of Pen 70/100 at different ageing conditions.

Fig. 7. Master curves of complex modulus and phase angle of PmB at different ageing conditions.