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Effects of different ageing methods on the chemical and

rheological properties of bitumen

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1   **Abstract:** Bitumen undergoes ageing, which leads to changes in its chemical and rheological properties, thus

2   becoming harder and more brittle in time. This study aims to compare the effects of different laboratory

3   ageing methods on chemistry and rheology of three bitumen types, i.e. a Pen 40/60, a Pen 70/100 and a

4   polymer modified bitumen (PmB). Four ageing protocols were applied: ageing at room temperature, oven

5   ageing, the Pressure Ageing Vessel (PAV), and the Rolling Thin Film Oven Test (RTFOT) combined with

6   PAV ageing. The effects of temperature, pressure, and ageing time were studied using dynamic shear tests

7   and infrared spectroscopy. The results highlight the relationship between chemistry and rheology of bitumen.

8   Bitumen hardening, which was revealed by an increase in complex modulus and a decrease in phase angle,

9   was reflected in the growth of specific chemical functional groups. Among all materials, soft bitumen

10   showed the greater tendency to oxidize. Different behaviour was observed for PmB that presented the

11   highest resistance against oxidation among the studied bitumens, even though the reaction with oxygen

12   caused the deterioration of the added polymer modifiers.

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

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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

43 contribute to the viscous response of bitumen (Lerfald 2000). The reaction of bitumen and atmospheric

44 oxygen leads to the growth of polar and aromatic molecules, which are able to reduce the mobility of

45 molecules to flow; hence bitumen undergoes hardening and embrittlement.

46   In literature, several studies investigated the changes of bitumen fractions when subjected to ageing.

47 It has been found that aromatics generate resin fractions, which in turn generate asphaltenes. On the other

48 hand, the concentration of saturates changes slightly due to their low chemical reactivity (Lesueur 2009). The

49 oxidation of bitumen fractions generates a number of functional groups such as ketones, sulfoxides,

50 dicarboxylic anhydrides, and carboxylic acids. Ketones are formed from specific aromatic molecules, which

51 have two adjacent benzylic carbon moieties. When those molecules are oxidized, first, they result in the

52 formation of dicarboxylic anhydride and then, ketones are made by condensation. Carboxylic acids are

53 produced in small amounts. On the other hand, sulfoxides are the result of organic sulphides oxidation,

54 which represent functional moieties of many types of asphalt (Petersen 2009).

55   The types of oxidation products are consistently the same for bitumen from different sources, but

56 their amount may differ especially between unmodified and polymer modified bitumen (Lu et al. 2008). In

57 reality, the concentration of each product and their tendency to oxidize are influenced by crude oil origin. As

58 sulphides are more reactive, sulfoxides have higher production rate and are formed faster than ketones. After

59 that, ketones are formed, which finally yield anhydrides and carboxylic acids. Lesueur (2009) stated that

60 sulfoxides are thermally unstable and they reach a constant level, which depends on initial sulphur content

61 and oxygen diffusion into the material. In contrast, ketones and carboxylic acids are more stable, but they do

62 not always reach an asymptotic value. Also, Lesueur (2009) indicated that field aged bitumen usually

63 achieves a constant value, while an asymptotic value is not reached when bitumen is laboratory aged. On the

64 other hand, Liu et al. (1996) showed that the rate of carbonyl formation becomes constant for all laboratory

65 aged bitumen after an initial higher rate period. More recently, Lu et al. (2008) confirmed the increase of

66 carbonyls and sulfoxides molecules after standard short- and long-term ageing protocols, namely after

67 Rolling Thin Film Oven Test (RTFOT) and Pressure Ageing Vessel (PAV) ageing. They compared the

68 formation of these functional groups for unmodified and Styrene-Butadiene-Styrene (SBS) modified bitumen

69 through infrared spectroscopy. Sulfoxides were observed to grow more in the neat standard bitumen.

70 Conversely, a greater presence of carbonyl was found for the modified material. The researchers attributed

71 this increase to both oxidation and degradation of polymers.

72 The rheological and physical characteristics of bitumen are strongly related to the chemical ones.

73 Ageing causes stiffening of the bitumen as shown by an increase of complex modulus and a decrease of

74 phase angle (Lu et al. 2008; Molenaar et al. 2010). Moreover, oxidation increases bitumen viscosity, which

75 depends on the type and strength of molecular interactions. Petersen (2009) reported that bitumens with high

76 content of metals, especially vanadium, show major sensitivity to viscosity. In addition, the values of

77 softening point and penetration grade change after oxidation. Lu et al. (2008) reported that the softening

78 point increases for natural bitumen, while the opposite trend was found for polymer modified materials. On

79 the contrary, the penetration value decreases with increasing ageing time.

80

81 **Research objectives**

82 This study aims to compare the effects of different laboratory ageing methods on the chemistry and rheology

83 of bitumen. The influence of temperature, pressure, and ageing time were studied using the Dynamic Shear

84 Rheometer (DSR) tests and Fourier Transform Infrared Spectroscopy (FTIR). Also, the properties of aged

85 bitumens were compared with those of the unaged fresh materials to study the susceptibility of the different

86 bitumen types to ageing.

87

88 **Experimental research**

89 To study the effects of different laboratory ageing methods on bitumen chemistry and rheology four ageing

90 protocols were applied: ageing at room temperature, oven ageing, Pressure Ageing Vessel (PAV) and

91 Rolling Thin Film Oven Test (RTFOT) combined with PAV ageing. The effects of temperature, pressure,

92 and ageing time on three bitumens types were studied by means of DSR and FTIR tests. Two replicate

93 samples of each bitumen type were tested at every ageing condition to determine statistically reliable results.

94 In all the cases analysed, similar results were obtained.

95

96 *Materials and sample preparation*

97   Three bitumen types were adopted throughout this study, two standard or neat bitumens and one polymer

98   modified bitumen. The standard materials varied with respect to their penetration grade; a Q8 Pen 40/60

99   bitumen and a Q8 Pen 70/100 bitumen were used. The Q8 polymer modified bitumen with a grade QmB

100 45/80 - 65 was obtained by the addition of Styrene-Butadiene-Styrene (SBS) polymers, which are often used

101 to enhance the durability and resistance of bitumen (Dondi et al. 2016). Table 1 lists the properties of the

102 materials.

103   Cylindrical bitumen samples were prepared according to the European Standard NEN-EN

104 12594:2014. The diameter of the samples was equal to 27.50 mm and their thickness was 2 mm. Bitumen, in

105 quantity lower than one liter, was heated in the oven for 120 minutes at temperature that did not exceed the

106 softening point of each specific bitumen type more than 100°C. The liquid bitumen was stirred and poured in

107 a silicon mould to cool down. Then, the mould was placed in a refrigerator for about 15 minutes. The

108 samples were finally demoulded and were ready for ageing in the lab.

109

110 ***Ageing methods***

111 Four ageing methods were applied, namely ageing at room temperature, oven ageing, ageing by means of the

112 Pressure Ageing Vessel, and an ageing protocol that included the combination of Rolling Thin Film Oven

113 Test and PAV ageing.

114   Ageing at room temperature was performed at five different time intervals of 5, 10, 15, 20 and 25

115 days. The average room temperature was 24.6°C. During room ageing the samples were not homogenized, as

116 this would require the application of heat that could affect the results. Oven ageing was carried out at 135°C

117 for 60 hours, and 5, 10, 15 days. A standard quantity of bitumen (90±3 g) was heated and poured into

118 aluminium containers forming a 1 cm thick layer. During ageing, bitumen was manually stirred, rotating the

119 trays clockwise and counter-clockwise once a day in order to encourage the homogeneous ageing of the

120 samples. The Pressure Ageing Vessel test was performed at standard conditions, i.e. ageing at 100°C

121 temperature and 2.1 MPa pressure for 20 hours, following the NEN-EN 14769:2005 European Standard.

122 Moreover, PAV test was realized at the same temperature and pressure but for a double ageing time (40

123 hours). Finally, the short- and long-term standard ageing procedures were combined; first the samples were

124 aged using the RTFOT according to the NEN-EN 12607-1:2014 European Standard followed by PAV at

125 standard conditions. The aforementioned ageing methods are listed in Table 2.

126

127 ***Test methods***

128 The effects of ageing were evaluated by means Dynamic Shear Rheometer tests and Fourier Transform

129 Infrared Spectrometry. The Perkin Elmer Spectrum 100 FTIR spectrometer was used in the Attenuated Total

130 Reflectance (ATR) mode to identify the chemical functional groups of the bitumens. The wavelength of the

131 reflected beam is characteristic of each element and indicates the presence of specific functional groups.

132 Using the ATR technique, sample preparation was simple. A small sample of material was taken using a

133 spatula and placed under the FTIR anvil. The FTIR spectrum was obtained in the spectral range between

134 4,000 and 600 cm^{-1} with a scanning resolution of 4 cm^{-1} averaging five scans for each measurement in order

135 to increase the signal-to-noise ratio of the measurements. Then the spectrum was normalized to allow the

136 quantitative analysis of the results.

137 The oxidation of bitumen was evaluated at specific bands of wavelengths, which can reveal the

138 formation of the characteristic oxidation products. Researchers have identified four specific wavelengths

139 where the changes due to ageing can be observed. Due to the complexity of the chemical composition of

140 bitumen a fixed peak cannot be found for bitumens especially if the origin of materials is different (Van der

141 Bergh 2011). For this reason, in this study, the effects of ageing were analyzed considering specific bands of

142 wavelength, as defined by Lamontagne et al (2001), and the corresponding area under those bands (Van der

143 Bergh 2011). The peak areas were evaluated using semi-quantitative analysis and then the four ageing

144 indices, namely the aromaticity, long chain, carbonyl and sulfoxide were determined, as presented in Table

145 3.

146 Bitumen rheology was characterized through DSR tests. The Anton Paar EC-Twist 502 device was

147 used to analyse the material response over a wide range of temperatures and frequencies that occur during

148 the pavement service conditions. First, the Linear Viscoelastic Range (LVE) of each bitumen type was

149 determined by means of amplitude sweep tests. The maximum strain value within the linear viscoelastic

150 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

151 strain amplitude values applied during the frequency sweep tests for each bitumen. The tests were performed

152 using the parallel plate configuration in a strain controlled mode, applying an oscillatory shear stress on a

153 sample of 1 mm thickness. The tests were performed at a range of frequencies from 10 Hz to 0.1 Hz and at

154 five temperatures, specifically at 10°C, 20°C, 30°C, 40°C and 50°C.

155

156 **Results and discussion**

157 *Fourier Transform Infrared Spectroscopy analysis*

158 The FTIR spectra were obtained in a wavelength range from 4,000 to 600 cm^{-1}. However, the changes due to

159 ageing can be found at wavelengths less than 1800 cm^{-1}, as shown in Fig. 1.

160   Fig. 2 shows the aromaticity and long chain indices for all bitumen types after the application of the

161 various ageing methods. The aromaticity index denotes the aromatization of bitumen and relates to the

162 increase of viscosity (Nivitha et al. 2016). The results show that the aromaticity index does not vary

163 significantly after ageing at room temperature for none of the three bitumen types. In contrast, oven ageing

164 seems to affect the aromatic fraction. The value of the aromaticity index increases in time for the polymer

165 modified bitumen, especially after five days of oven ageing. For the neat bitumens, the aromatic fraction

166 shows an increase after five days of oven ageing similar to the PmB, but then remains relatively constant.

167 The standard PAV method does not influence significantly the value of the aromaticity index compared to its

168 value before ageing. The application of the extended PAV protocol results in an increase of the aromaticity

169 index similar to this of prolonged oven ageing.

170   Nivitha et al. (2016) observed a decrease of the long chain index with increasing ageing time.

171 Similarly, Fig. 2 shows that the long chain index decreases with extended oven ageing for all bitumens.

172 Depending on the bitumen type, the index seems to decrease with ageing time (for PmB and Pen 70/100) or

173 reaches a steady state after five days of oven ageing (Pen 40/60). The evolution of the long chain index does

174 not show a specific trend with time when aged at room temperature.

175   On the contrary, Fig. 3 shows that the values of the carbonyl and sulfoxide indices increase during

176 ageing; the extent of increase depends on the ageing method applied to the bitumen samples. The carbonyl

177 index denotes the formation of ketones, dicarboxylic anhydrides and carboxylic acids due to the reaction

178 between carbon and oxygen (C=O), whereas the sulfoxide index denotes the S=O stretching due to the

179   oxidation of sulphides. Both indices are identified as key parameters when studying bitumen ageing, as the

180   carbonyl groups and sulfoxides are the most important oxidation products.

181   It is interesting to note that the carbonyl index has zero value after room ageing, regardless of the

182   duration of ageing and the bitumen type. On the other hand, ageing in the oven at 135°C causes an increase

183   of the carbonyl index. The duration of oven ageing influenced the formation of carbonyl compounds, as

184   indicated by the growth of the carbonyl index. After 60 hours of oven ageing, the carbonyl index of both neat

185   bitumens remains zero. After 5 days of oven ageing, a slight increase is observed for the harder Pen 40/60

186   bitumen, whereas a higher value is obtained for the Pen 70/100. However, after 10 days of oven ageing the

187   value of the carbonyl index increases substantially for both bitumen types and becomes one order of

188   magnitude higher than its value at five days. Overall, the formation rate of carbonyl compounds is higher for

189   Pen 70/100 as indicated by the absolute values of the carbonyl index, which are one order of magnitude

190   higher than those of the harder bitumen. The formation of carbonyl compounds for the PmB occurs after 10

191   days of oven ageing, unlike for the unmodified bitumens. The delay in carbonyl formation can be attributed

192   to the inherently low susceptibility of polymer modified bitumens to higher temperatures.

193   The production of sulfoxides does not follow the same trend. Sulfoxides are formed to some extent

194   when the samples are aged at room temperature, indicating that the natural content of sulphur reacts with

195   atmospheric oxygen even at lower temperatures. It is, therefore, shown that the sulfoxides (S=O) have a

196   higher production rate than the carbonyls. This finding verifies the higher rate production of sulfoxides than

197   ketones reported by Lesueur (2009).

198   Sulfoxides in Pen 70/100 bitumen are also formed at a higher rate compared to Pen 40/60 as

199   indicated by the sulfoxide index. The value of the sulfoxide index for Pen 70/100 changed by 33%-40% after

200   ageing at room temperature and 52-62% after oven ageing compared to its value at unaged conditions. In

201   contrast, the sulfoxide index for Pen 40/60 increased only by 12% after room ageing and 11-16% after oven

202   ageing compared to the reference unaged value. These findings indicate that the soft bitumen is more

203   susceptible to oxidative ageing than the harder Pen 40/60 bitumen. For the unmodified bitumens, the

204   application of the standard PAV method, combined or not with the standard RTFOT method, results in the

205   growth of both the sulfoxide and carbonyl index. From a comparison between the O60h protocol and the

206   PAVS protocol, it can be observed that the application of pressures higher than the atmospheric pressure

207 promotes the formation of carbonyl compounds, even though the PAVS ageing was performed for less time

208 and at lower temperature than O60h ageing after which no carbonyls were produced.

209   On the other hand, the sulfoxide index for the PmB did not vary considerably with ageing time at

210 room temperature, whereas oven ageing caused an increase in its value after 5 days of ageing. The

211 application of high temperature and pressure (PAVS, PAVM and RTFOT+PAVS ageing methods) affected

212 the growth of sulfoxides, but did not increase significantly the amount of carbonyls when using the two

213 standard ageing protocols. It was observed that the application of PAVS and RTFOT+PAVS ageing resulted

214 in a minor increase of the carbonyl index for the PmB, while the extended PAVM protocol had a significant

215 effect on the carbonyl index, possibly due to the prolonged ageing time. The presence of styrene and

216 butadiene copolymers in the PmB is detected at 700 cm^{-1} and 968 cm^{-1} wavelength, respectively (BRRC

217 2013). The polymer peaks after the application of each ageing method are listed in Table 3. The results show

218 that the styrene copolymer degrades with ageing, especially after oven ageing and the PAV ageing protocols.

219   Among the various ageing methods the PAVM and the prolonged oven ageing were the most

220 effective ageing protocols, as indicated by the changes in the carbonyl and sulfoxide indices. Both the

221 carbonyl and sulfoxide indices were found to increase during ageing. However, it has been observed that the

222 formation of carbonyl compounds was mainly the result of applying high temperature. It is therefore

223 suggested that the carbonyl index and the relative increase of the sulfoxide index (compared to a reference

224 unaged value) are considered together when characterizing ageing in bituminous mixtures; especially in the

225 case of bitumen recovered from asphalt pavements, where such high temperatures do not usually take place,

226 using only the carbonyl index as ageing indicator may lead to incorrect conclusions with regard to the

227 bitumen susceptibility to ageing. The graph in Fig. 4 compares the development of oxidation products after

228 three ageing methods, namely after 25 days of room ageing, 15 days of oven ageing and the application of

229 PAVM ageing. The formation of oxidation products varies with the ageing method for all bitumens.

230 Nevertheless, the results confirm the greater sensitivity of Pen 70/100 bitumen to oxidize.

231

232 ***Dynamic shear rheometer test results***

233 Oxidative ageing is known to alter the rheological properties of bitumens, causing an increase in complex

234 modulus and a decrease in phase angle. Every bitumen type responds in a different way to ageing, and

235   therefore the changes in physical properties can be different, mainly due to its dependency on oxidation

236   kinetics (Juristyarini et al. 2011). Fig. 5 and Fig. 6 show the master curves of Pen 40/60 and Pen 70/100

237   bitumens, respectively, at unaged state and after the application of the R25d, O15d, RTFTO+PAVS and

238   PAVM ageing protocols.

239   It can be observed that the most noticeable changes in complex modulus due to ageing were recorded

240   at low frequencies as the bitumen was in the rubbery flow region, whereas minor changes were observed at

241   high frequencies (glassy transition region). Similar to the results obtained from the FTIR measurements, it

242   was observed that oven ageing, at 135°C for 15 days, affected the rheology of bitumens more than the

243   combined effects of high temperature and pressure. Again, ageing at room temperature for 25 days did not

244   result in significant differences with respect to the rheological response of fresh (unaged) bitumen. It seems

245   that oxidation took place, but in a very slow rate, confirming that bitumen reacts slowly with atmospheric

246   oxygen (Herrington 2012). The phase angle of the unmodified binders decreased considerably with ageing,

247   indicating an increase in elasticity of bitumen and a reduction of its flow characteristics. Oven ageing, in

248   particular, caused a great increase in phase angle especially at low frequencies (high temperatures), which in

249   combination to the increase of complex modulus, is an indication of embrittlement of the material.

250   Fig. 7 shows the complex modulus and phase angle master curves for the PmB. The complex

251   modulus of PmB increased with ageing, but to a less extent if compared to the unmodified bitumens. It was

252   observed that after 15 days oven ageing the complex modulus, at low frequencies, increased by one order of

253   magnitude. Overall, the rheological response of the PmB after oven ageing did not differ significantly with

254   its response after the application of the PAVM and PAVS+RTFOT protocols, in contrast to what was

255   observed for the unmodified binders. This possibly occurs due to the high temperature susceptibility of the

256   polymer modified bitumen, which can undergo higher temperatures for prolonged ageing times.

257   The phase angle master curve at unaged condition shows a characteristic plateau in the intermediate

258   frequency area. This feature actually shows the presence of polymer into the bitumen chemical structure.

259   This characteristic plateau in the phase angle master curves is maintained after 25 days of room temperature

260   ageing. However, the application of high temperature for prolonged time (O15d) or combinations of high

261   temperature and pressure (PAVM and RTFOT+PAVS) caused a smoothening of the curve, as shown in Fig.

262   10. This result may be explained by the fact that degradation of the polymer modifier can occur after the

263 specific ageing protocols. The FTIR measurements support this hypothesis as it was observed that the

264 styrene copolymer peak degraded with ageing, especially after the application of the O15d and PAVM and

265 RTFOT+PAVS protocols. In general, based on the rheological properties, the PmB was found to have

266 greater resistance to the oxidation processes, while Pen 70/100 bitumen was highly sensitive to ageing.

267

268 **Conclusions**

269 This study aimed to compare the effects of different laboratory ageing methods on the chemical and

270 rheological properties of unmodified and SBS modified bitumens. The evolution of the chemical properties

271 during ageing was monitored using the indices that correspond to aromaticity and long chains, as well as to

272 the formation of carbonyls and sulfoxides. Moreover, the characteristic peaks of the modifiers were

273 considered. The changes in rheology were evaluated on the basis of complex modulus and phase angle

274 master curves.

275 The influence of high temperature was clearly observed for unmodified bitumens when compared to

276 the polymer modified bitumen in terms of both thermo-sensitivity reduction (Vignali et al. 2016) and ageing

277 response. The ageing indexes and the rheological response of both neat bitumen types, Pen 40/60 and Pen

278 70/100, demonstrate that high temperatures applied for a prolonged time ($\geq$10 days) influence more the

279 bitumen response than the combined effects of high temperature and pressure due to PAV and RTFOT. For

280 the polymer modified bitumen, though, oven ageing at high temperature did not result in large differences in

281 its rheological response when compared to the response after the application of the PAVM and

282 PAVS+RTFOT protocols, possibly due to the high temperature susceptibility of the polymer modified

283 bitumen. Nevertheless, the characteristic plateau in the phase angle master curve at unaged condition,

284 denoting the presence of polymer modifiers, was smoothened out after the application of high temperature

285 for prolonged time or combinations of high temperature and pressure. It was hypothesized that the

286 aforementioned ageing conditions degrade the polymer modifier; the evolution of the characteristic FTIR

287 peaks of the modifiers confirmed this hypothesis.

288 The aromaticity index and the long chains index did not vary significantly after ageing at room

289 temperatures; nevertheless, the application of high temperatures and pressure resulted in a decrease of the

290 long chain index and an increase of the aromaticity index. In some cases, no specific trend was observed

291 with respect to ageing time or temperature. In contrast, both the carbonyl and sulfoxide indices increased

292 with ageing. Carbonyls formed at a slower rate than the sulfoxides. Ageing at room temperature did not

293 stimulate carbonyl formation for any of the bitumens; the carbonyl index remained equal to zero. After 60

294 hrs of oven ageing at high temperature for the unmodified bitumens (or five days for the polymer modified

295 bitumen) carbonyl compounds were formed, as indicated by the growth of the carbonyl index.

296   Similarly, ageing at room temperature did not influence the rheological properties of the bitumens.

297 Overall, bitumen hardening, which was revealed by an increase in complex modulus and a decrease in phase

298 angle, was reflected in the growth of specific chemical functional groups. The polymer modified bitumen

299 showed a highest resistance against the oxidation, thus against stiffening and embrittlement, than neat

300 standard bitumens. Among the unmodified bitumens, the soft Pen 70/100 bitumen exhibited the greater

301 tendency to stiffen compared to the harder Pen 40/60 bitumen.

302

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357

358   **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

359

360 **Table 2**. Applied Ageing Methods

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

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362

363   **Table 3.** Indices calculated for all bitumens

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

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$A_{1670\text{-}1535}/\sum A$

$A_{734\text{-}710}/A_{1376}+A_{1460}$

$A_{1753\text{-}1660}/\sum A$

$A_{1047\text{-}995}/\sum A$

$\sum A = A_{(2953,2862)}+A_{1700}+A_{1600}+A_{1460}+A_{1376}+A_{1030}+A_{864}+A_{814}+A_{743}+A_{724}$

368

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

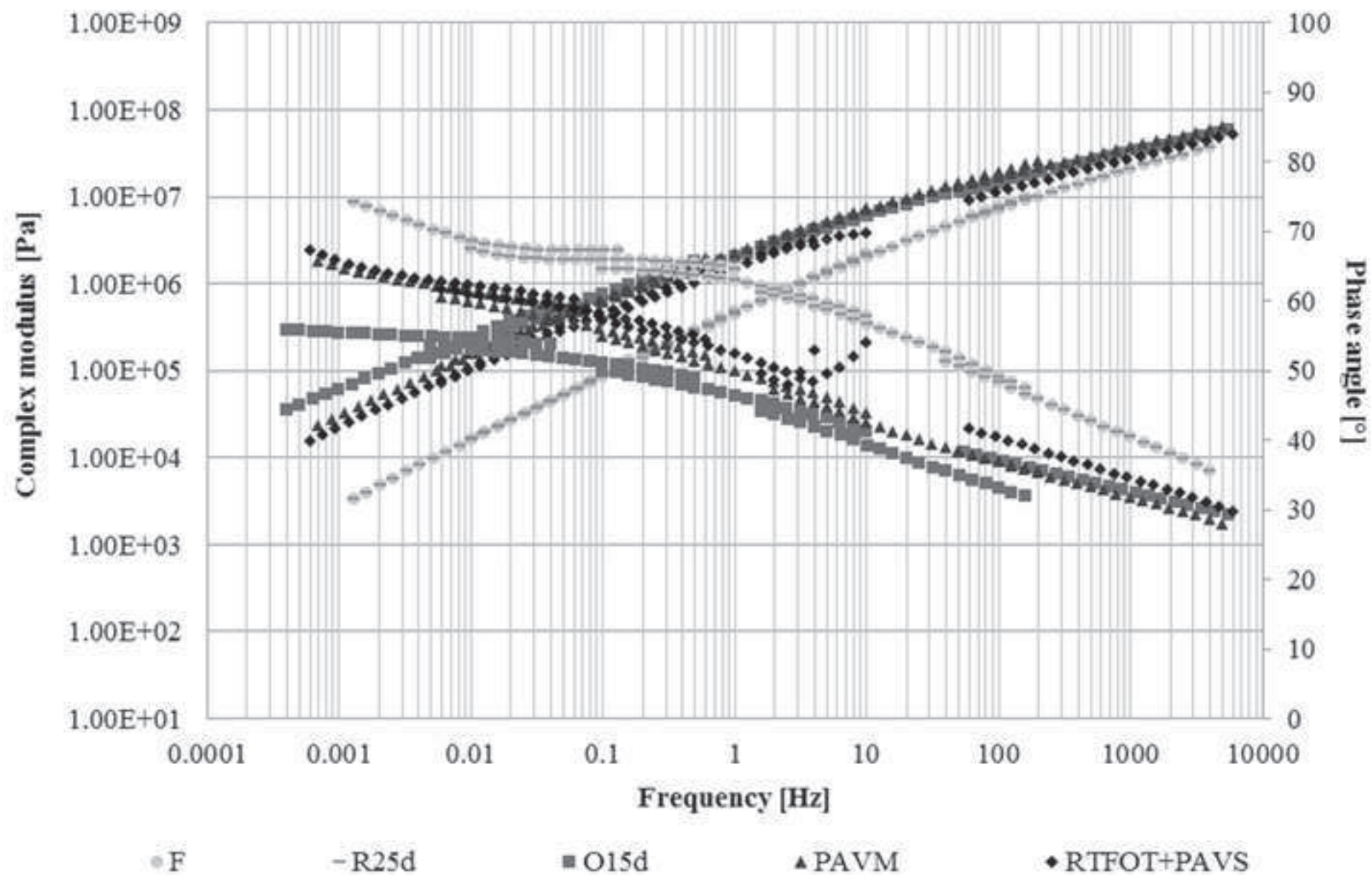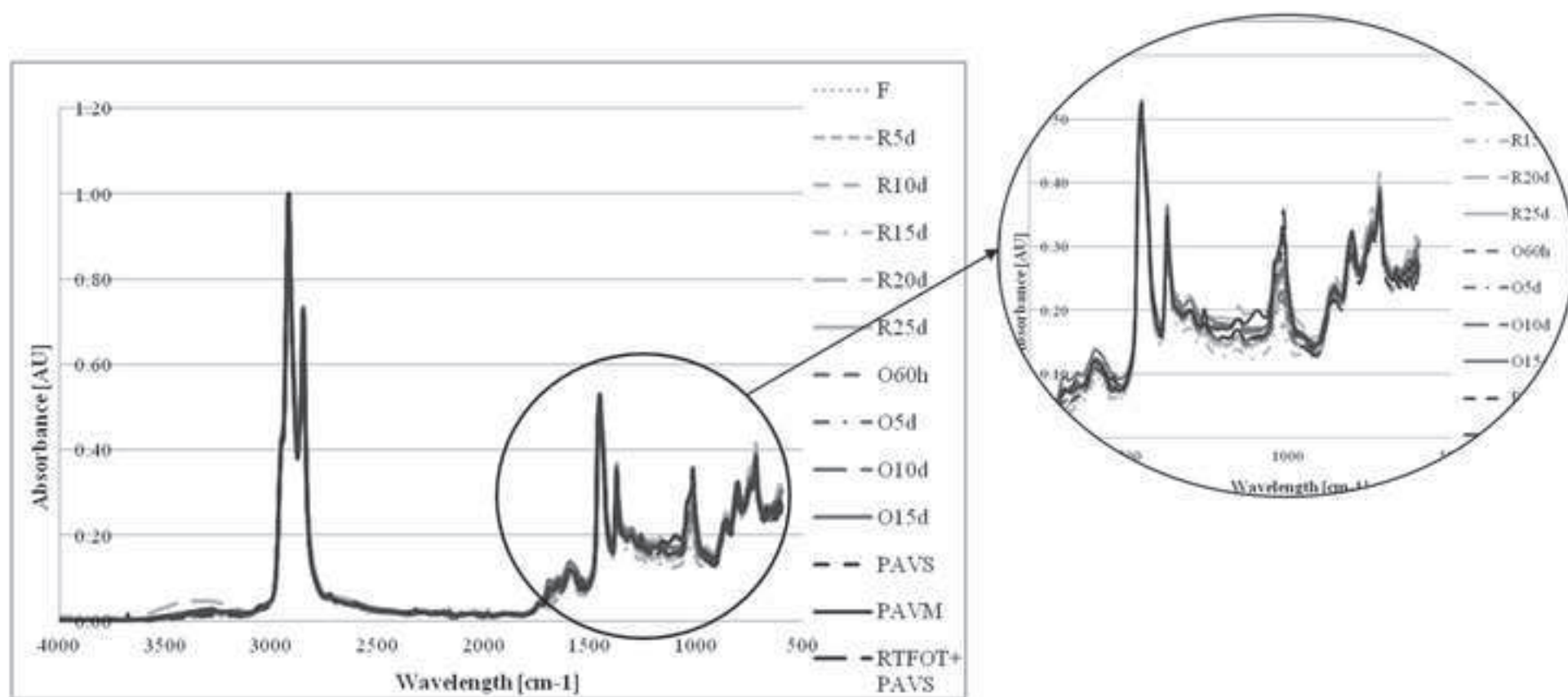| Ageing method	Styrene peak [700 cm-1]	Butadiene peak [968 cm-1]
fresh (unaged)	0.3436	0.2102
R5d	0.2995	0.1954
R10d	0.3069	0.2067
R15d	0.3001	0.1862
R20d	0.2726	0.1859
R25d	0.2877	0.1890
O60h	0.3219	0.2137
O5d	0.3156	0.2173
O10d	0.3006	0.2147
O15d	0.3085	0.2150
PAVS	0.3097	0.2179
PAVM	0.3036	0.2233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

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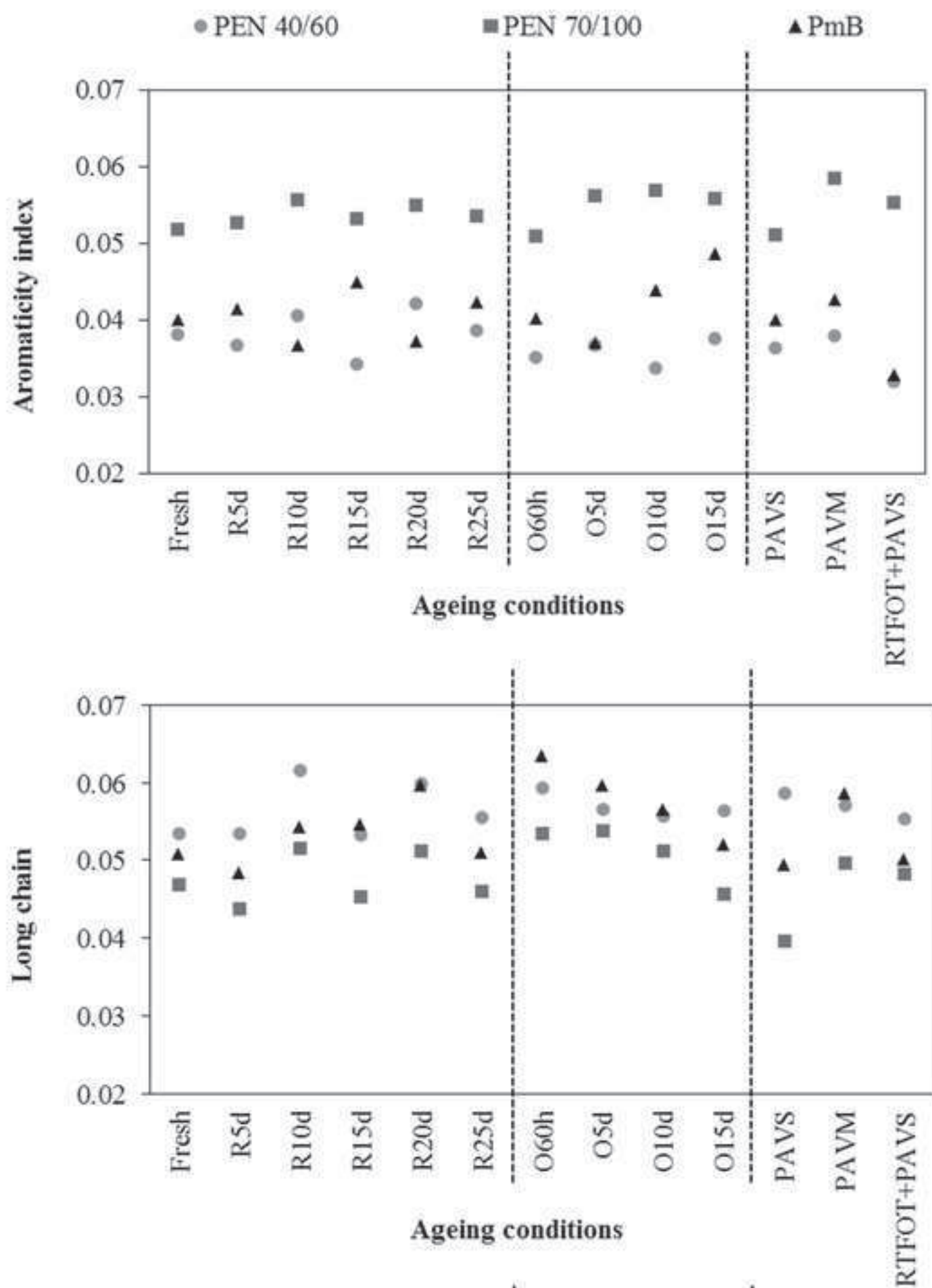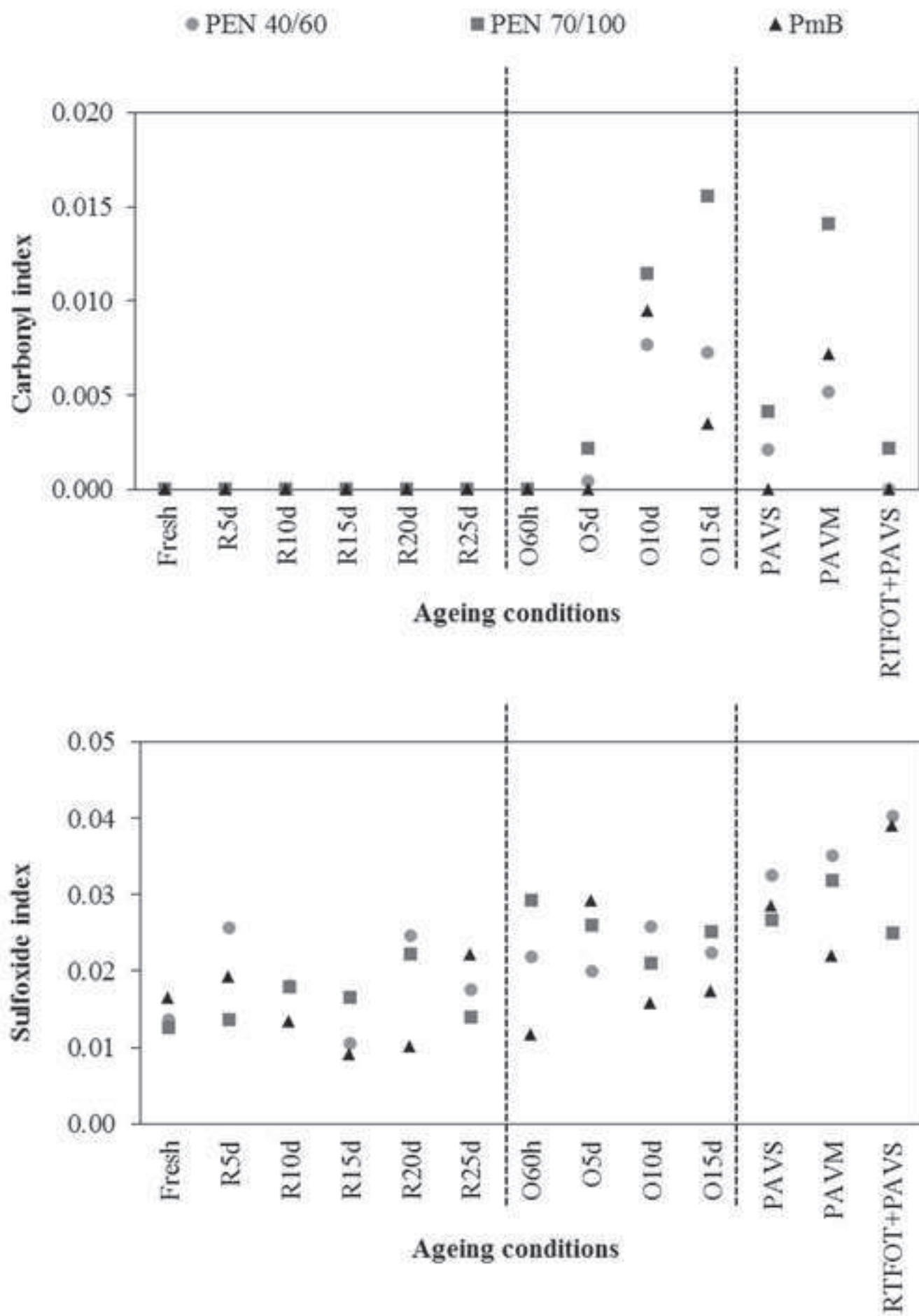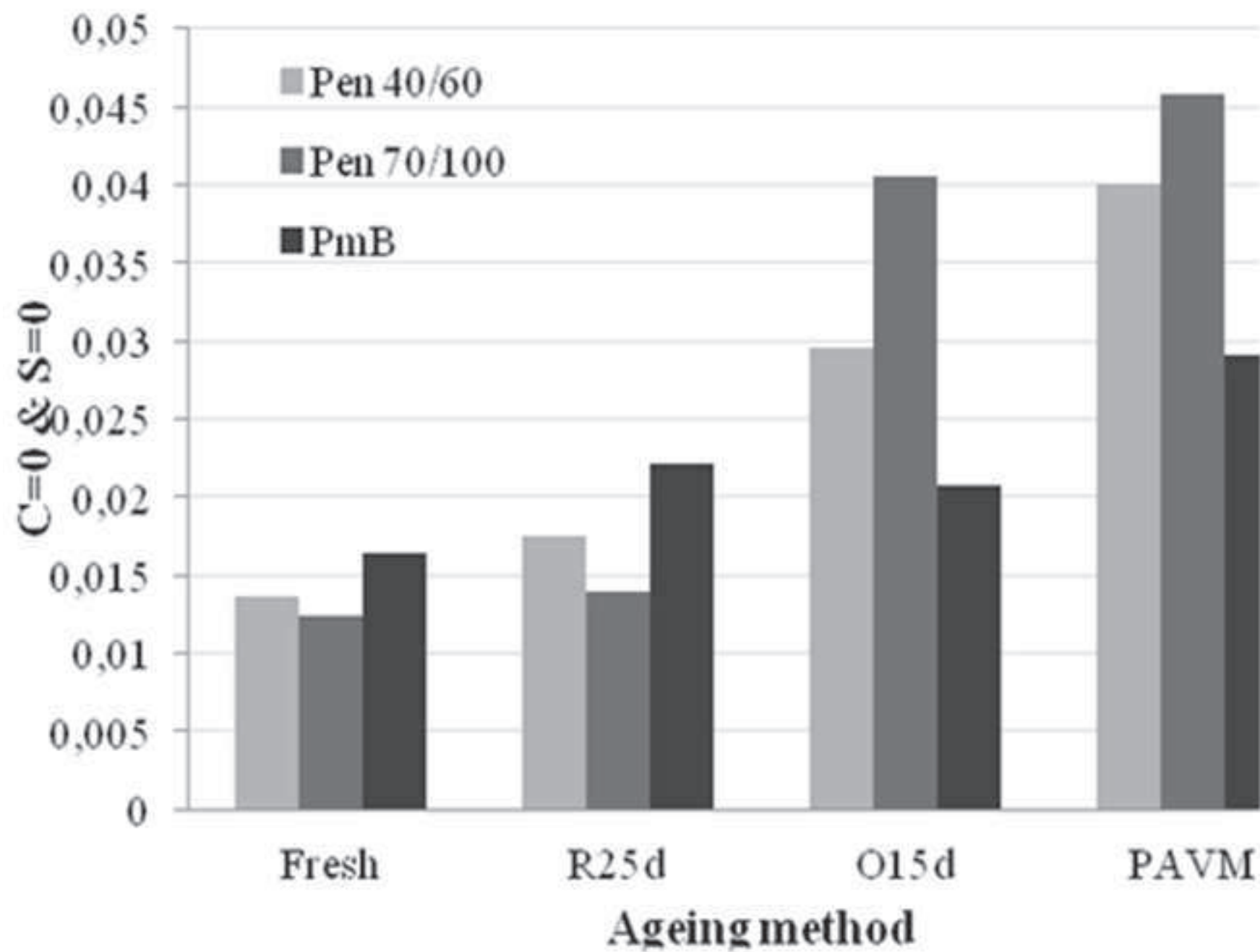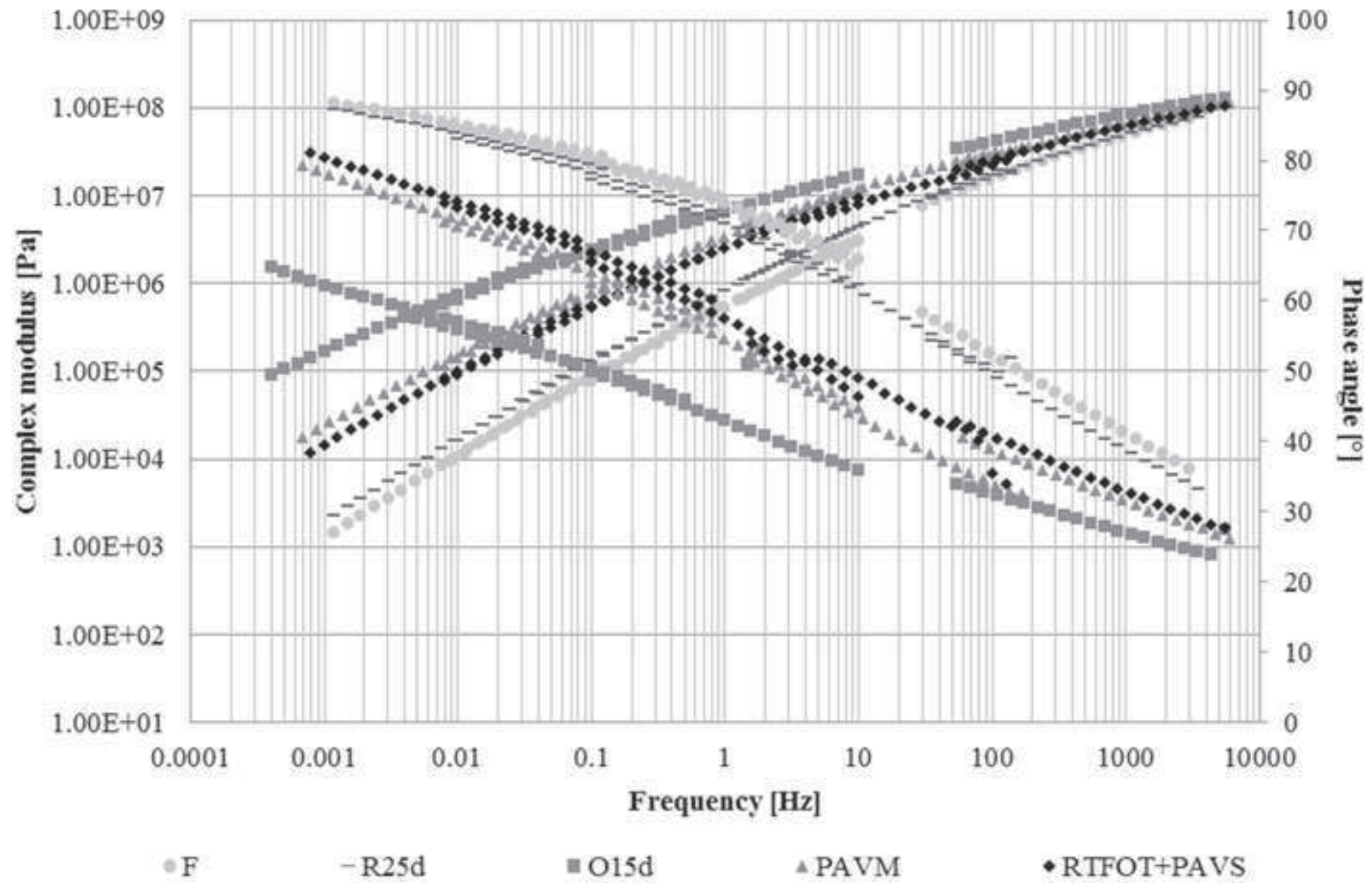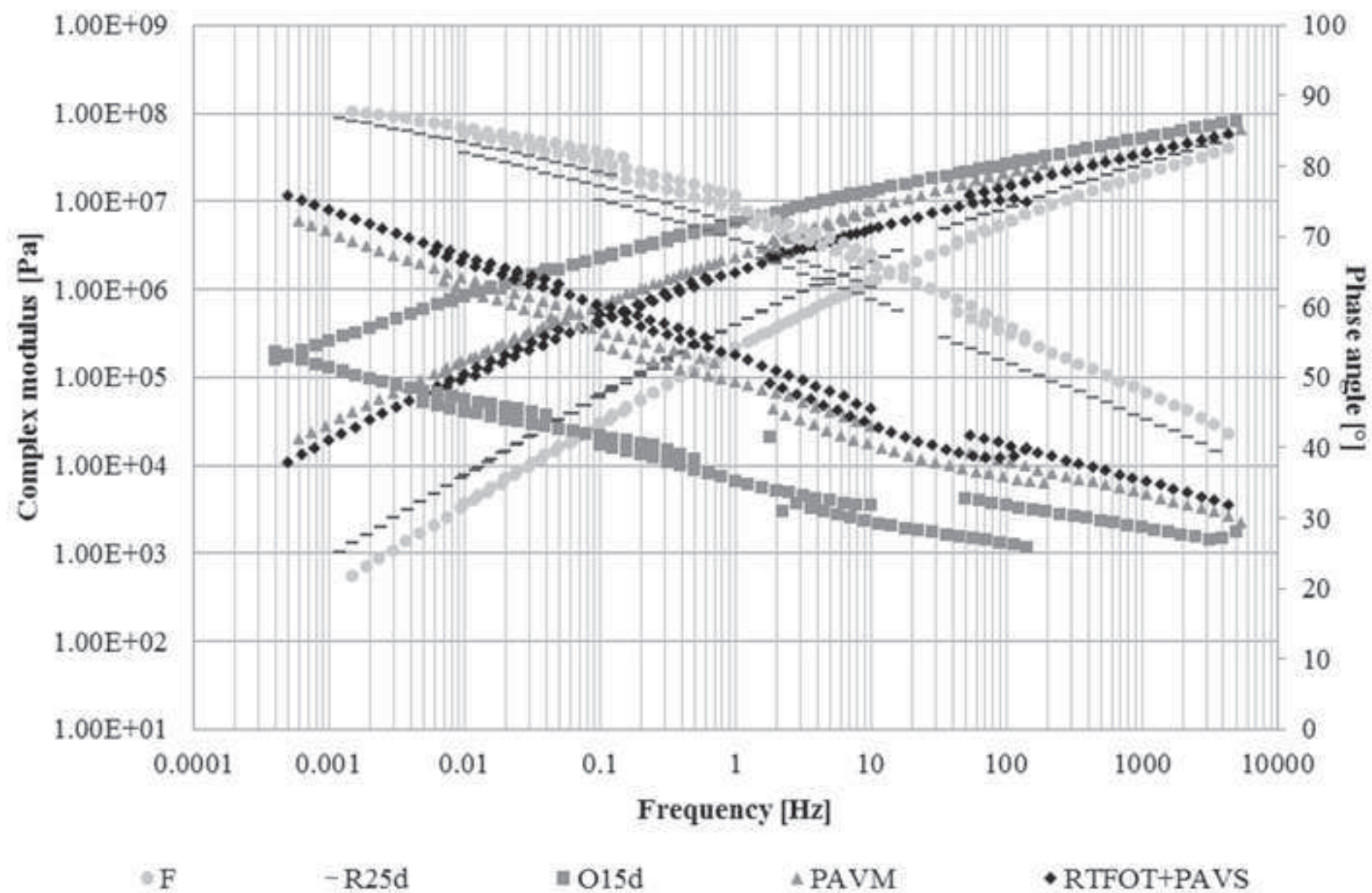
List of figure captions

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.