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Evaluation of Epoxy Modification in Bitumen

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Abstract: In epoxy-bitumen systems, temperature contributes to the development of physiochemical and mechanical characteristics during curing (chemical hardening) and at the long-term service (oxidative aging) of pavement structures. Hardening (i.e., chemical or oxidative controlled) is a complex phenomenon in epoxy-modified binders and the in-depth exploration of incorporating epoxy chemistry in bitumen is needed to understand the evolution of the properties of these binders in time. Within this framework, changes in two different diluted epoxy-modified binders after oven-hardening for various time scales were analysed by means of Fourier transform infrared spectroscopy, modulated dynamic scanning calorimetry and dynamic shear rheometry. The chemical, thermal and mechanical properties of hardened binders were compared showing remarkable differences in their response under various conditions. The degree of aging was dependent on the level of epoxy modification in bitumen. It was found that the sulfoxide compounds are the most representative index for assessing the oxidative-controlled hardening of epoxy-modified bitumens. The phase angle gives useful information for assessing the long-term aging of modified binders demonstrating a linear relationship between the phase angle and sulfoxide index changes with respect to oxidative hardening. The improved performance (i.e., higher tensile strength, flexibility and enhanced longevity) of newly modified binders was demonstrated as well. Overall, the enhanced resistance against aging in combination with the superior mechanical characteristics when the epoxy modification is implemented in bitumen promises a very effective technology for developing long-lasting pavement materials.

39 **INTRODUCTION**

40 Studies of bitumen modification technologies have been undertaken in the past and
41 predominantly thermoplastic polymers (i.e., block polyolefins co-polymers) are nowadays
42 extensively used as modifiers to enhance the material durability both at low and high
43 temperatures (1-4). Nevertheless, the exploration of new modification approaches has been at
44 the forefront of pavement engineering research efforts due to the increasing demand on
45 developing pavement materials with improved long-lasting characteristics.

46 The use of epoxy modifiers has attracted the attention of the pavement scientists and
47 practitioners (5-10). Initially, the epoxy modifiers were utilized to minimize the permanent
48 deformation of bituminous materials because the thermoset nature of epoxies guarantees
49 excellent rut resistance (5). It was also suggested that use of polymeric structure of epoxy in
50 the bituminous matrix can enhance the resistance against aging of bitumen (10). However,
51 despite experience of practitioners on implementing epoxy modifiers in bituminous materials,
52 a general lack of knowledge still exists about the impact of these modifiers on the
53 physiochemical characteristics and the long-term performance of bitumen. Properties, such as
54 tensile strength or glass transition temperature, have been evaluated in the past (11-18) but
55 with limited studies of chemistry-related hardening phenomena, such as curing (i.e.,
56 chemical-controlled hardening - CH) or aging (i.e., oxidative-controlled hardening -OH).

57 The addition of epoxy modifier in bituminous binders is a relatively new modification
58 technology and the crucial epoxy polymerization-induced changes of the epoxy-bituminous
59 materials are not fully understood. Different phenomena take place when different amounts
60 of epoxy are incorporated into bitumen and they are dependent on the material hardening
61 conditions (20, 21). The concentration of epoxy resinous part in bitumen controls the
62 microstructural characteristics of modified blends and might influence the longevity of these
63 materials. In this paper, the chemical compounds and their reaction products generated under
64 various hardening conditions were studied to reveal the time dependency of molecular
65 microstructures of modified bitumen. Special attention was given to the evaluation of
66 physiochemical characteristics and the mechanical properties of epoxy bituminous binders.
67 Overall, the studies reported in this paper focused on establishing a testing framework
68 specially designed for epoxy-bitumens by linking the chemistry-related phenomena with their
69 mechanical performance.

70

71 **MATERIALS AND PREPARATION**

72 The epoxy-based modifier is a commercial product supplied by ChemCo Systems, USA and
73 named epoxy asphalt. This modifier is formulated from two liquid parts free from solvents;
74 (i) the part A (epoxy resin formed from epichlorhydrin and bisphenol-A) and (ii) part B
75 (blend of fatty acid hardening agent and 70 pen bitumen). When part A and B (both reacting
76 systems) are mixed into bitumen as modifying elements, the dispersion of the modifier phase
77 inside the bitumen is achieved. In reality, the monomers of part B react with the epoxide
78 groups of part A to produce covalent bonds in bitumen and the molecular chains are
79 crosslinked through the polymerization process.

80 In this study, all the samples were prepared by mixing part A and B at weight ratio of
81 20:80, according to the supplier. Unless otherwise stated the two components, part A and B,
82 were oven-heated separately for 1 hour, to 85°C and 110°C, respectively. After that one hour,
83 they were mixed together for approximately 10 to 20 seconds and this epoxy modifier was
84 mixed further with an already pre-heated unaged 70-100 pengrade bitumen at 120°C, on the
85 basis of the supplier's recommendations. Two epoxy modification levels of bitumen were
86 studied; by adding 20 and 50 %wt. of modifier with replacing equivalent amount of bitumen.
87 In other words, two epoxy-modified bituminous binders were formed with weight ratio of
88 20:80 (EB20) and 50:50 (EB50) of epoxy and bitumen, respectively. The study of these two

89 modification levels is linked also with an effort to generate economically feasible and long-
90 lasting paving materials since the initial price of supplied system, named epoxy modifier, is
91 high. Finally, all the prepared samples were placed in a refrigerator at -10°C to prevent any
92 further reaction.

93 The hardening of the binders was simulated in a draft oven under atmospheric pressure
94 over various lengths of time. At a temperature of 130°C and at 1.0-kPa hardening times of 0,
95 2, 5, 8, 24, 120, 240 and 480 hrs, were compared. The same materials were aged in a
96 pressure-aging vessel (PAV) on pans with 140-mm in diameter and 3-mm film thickness at
97 2.1-MPa pressure with oxygen (AASHTO MP1). PAV aging time for 100°C was 20 hrs.
98 After each hardening period, the physiochemical and mechanical properties were measured as
99 function of time through Fourier Transform Infrared (FTIR) spectroscopy, modulated
100 dynamic scanning calorimetry (MDSC) and dynamic shear rheometer (DSR). The testing
101 methods used for this research are presented in the following sub-sections.

102

103 **EXPERIMENTAL METHODS**

104

105 **Chemical and Physical Characteristics during Hardening**

106 The chemical properties of the hardened epoxy modified bitumens (EBs) were determined
107 with a Perkin–Elmer Spectrum FT-IR spectrometer equipped with an Attenuated Total
108 Reflectance (ATR) fixture. The hardening of materials was analysed after the time intervals
109 used. The FTIR spectrometer was used to investigate the change of the molecular structure of
110 the binders after each hardening time and to provide information about CH and OH of EBs.
111 The FT-IR spectra with wavenumber from $4,000$ to 600 cm^{-1} were recorded and collected for
112 all the samples. A certain amount of material was placed directly on the ATR crystal pedestal
113 and pressed with a constant force to ensure proper contact to the surface. A minimum of three
114 sub-samples were investigated for each sample and 20 scans per sub-sample were performed
115 with a fixed instrument resolution of 4 cm^{-1} (22, 23). **Fig. 1(a)** shows the FT-IR spectra of
116 base (EB0) and epoxy modified bitumen (EB50) recorded after 480 hrs at 130°C .

117 For OH of bitumen, the carbonyl ($1753\text{--}1660\text{ cm}^{-1}$) and sulfoxide index ($1047\text{--}995\text{ cm}^{-1}$)
118 are normally used to follow the aging in bitumen (24, 25). Their values were calculated by
119 using the area method representing the extent of age. The calculation is performed by
120 dividing the area under a specific location of the spectrum by the sum of other specific areas.
121 However, carbonyl groups ($\text{C}=\text{O}$) play an important role in the CH hardening of EBs as well.
122 During CH, oxirane groups ($\text{C}_2\text{H}_4\text{O}$) (at 917 cm^{-1}) react with the carbonyl acid group
123 (RCOOH) (at 1709 cm^{-1}) resulting into ester (RCOOR'') (at 1735 cm^{-1}) and ether (ROR') (at
124 1040 cm^{-1}). The potential contribution of methylene (H_2C) (3050 cm^{-1}) is not considered in
125 these cases. Fundamental analysis was performed using the absorbance intensity method of
126 peak difference (**Fig. 1(b)**) after the CH and OH hardening times.

127 Besides the chemical changes in bitumens under various conditions, the materials also
128 undergo microstructural transformations. A parameter that describes these temperature-
129 related transformations is the glass transition temperature (T_g). Bitumens show glassy
130 behavior below T_g , the rubbery characteristics could be shown above T_g . Previous studies
131 have shown a range of T_g values for epoxy-bitumens from -8 to 50°C (11-16), with neat
132 binders to show a range between -40 to 0°C (19).

133 In this study, in addition to chemical evaluation of involving compounds through CH, also
134 the phase transition temperature T_g of EBs was measured by MDSC under a nitrogen
135 atmosphere with $40^{\circ}\text{C}/\text{min}$ heating rate from -50 to 200°C . When the temperature of 200°C
136 was reached the samples were kept at this temperature for 2 min. MDSC is a thermal analysis
137 technique to determine the temperature and the heat flow associated with material transitions
138 as function of temperature and time. After the preparation and hardening of samples, they

139 were sealed in aluminum pans, and the CH behaviour was assessed by non-isothermal
140 experiments. The peak and mid-point of the heat flow shift denotes the T_g of materials. At
141 least two measurements were performed in each sample. Samples were hardening at different
142 hardening times from 0 to 180 min of 60 min time step. The MDSC curves of the studied EBs
143 during the heating processes are shown in **Fig. 2**, where T_g was characterised as the
144 temperature at which the first slope alteration took place, which coincides to an endothermic
145 peak in the first derivative plots.

146

147 **Mechanical Characteristics during Hardening**

148 To investigate the evolution of mechanical characteristics during curing (i.e., CH), the
149 complex modulus at 10 Hz was measured for a time window between 0 to 180 min at the
150 chosen hardening temperature of 130°C under isothermal conditions. DSR measurements
151 were performed using the parallel plate test configuration with disposable plates of 25-mm
152 diameter, and 1-mm sample thickness.

153 Additionally, viscoelastic characteristics, such as complex modulus and phase angle, were
154 used as reliable indicators for describing the aging behaviour (i.e., OH) of crosslinked epoxy
155 within the bitumen. Isothermal frequency sweep measurements were performed using a
156 dynamic shear rheometer (DSR, Anton Paar, EC Twist 502) at different temperatures that
157 ranged from -10 to 60°C. The parallel plate testing geometry was used as well to evaluate the
158 viscoelastic properties of the different binders after different hardening periods. Plates of 8-
159 mm diameter with a 2-mm gap were used at temperatures below of 20°C, while at temperature
160 above 30°C plates of 25-mm diameter with a 1-mm sample gap were used. The properties
161 were measured at frequencies of 0.1-10 Hz at temperature steps of 10°C from -10 to 60°C.
162 Sample was placed onto the bottom plate at the desired test temperature ($\pm 0.1^\circ\text{C}$). The
163 samples of base binder were treated in the same way and master curves were constructed. For
164 the master curves, the time-temperature superposition model was used to shift all
165 temperatures to a reference temperature of 30°C.

166

167 **Performance under Monotonic and Cyclic Loading**

168 The tensile strength has been investigated in the past showing various strength values from
169 1.25 to 9.90 MPa at standard test conditions (11, 13-18). In this paper, after curing, the
170 strength of these binders was determined under controlled isothermal temperature conditions
171 at 0°C. The samples were prepared, poured into a Teflon mould, and taken out of the storage
172 container any excess material was trimmed of and fixed with clamps in the DSR. The
173 cylindrical sample (height 10-mm, diameter 6-mm) was loaded in tension with a
174 displacement speed of 0.05 mm/s. The tensile strength was calculated on the base of the
175 sample geometric configuration and the calculated value can be used to compare the results
176 of different modifications with bitumen.

177 Finally, the DSR was used to assess the long-term performance of epoxy binders via a
178 shear fatigue test, since the ultimate scope of incorporating this type of modifier is to increase
179 the longevity of bituminous materials. The DSR testing geometry of 8-mm diameter was used
180 with 2-mm gap and time sweep tests at a constant temperature of 0°C and a frequency of 10
181 Hz were performed at three different shear stress levels (i.e., 0.4, 0.5 and 0.6 MPa). At each
182 stress level, three fatigue tests were done for each modification. A decrease of the shear
183 modulus to 50% of its initial value was used as criteria to determine the load repetitions till
184 failure.

185 RESULTS AND DISCUSSION

187 Oxidative controlled Hardening

188 In general, the properties of EBs are linked to specific changes in their chemical structure.
189 Initially, the transition borders from CH to OH phenomena, and the initiation of aging, were
190 identified by measuring the carbonyl and sulfoxide components.

191 **Fig. 3(a)** shows the carbonyl content calculated with area method as a function of oven-
192 hardening time at 130°C for the studied binders. Along with the carbonyl content, the change
193 of sulfoxide due to age hardening was evaluated with the same method as well, and the
194 results depicting the relationship of sulfoxide over different times for EB0, EB20 and EB50
195 are shown in **Fig. 3(b)**. At high time lengths, both sulfoxide and carbonyls can indicate OH.
196 These compounds increase as hardening time increases and the results gave a similar
197 tendency for all samples with a lower hardening effect for the modified binders. Therefore, it
198 seems that the modified binders are more resistant against aging with EB50 showing the
199 lowest OH sensitivity, see **Fig. 3(b)**. EB50 shows a lower sulfoxide index than the base
200 bitumen (EB0). The carbonyl and sulfoxide compounds of EB0 increase more rapidly than
201 EB20 and EB50, and as consequence, higher epoxy modification levels provide lower aging
202 indices. In addition to oven-hardening simulations, the long-term performance of EBs after the
203 PAV test seems promising as well when the sulfoxide index is used. According to the PAV
204 results, despite the inconsistencies of carbonyls generated from oven and PAV hardening (**Fig.**
205 **3(a)**), the sulfoxide compounds are equivalent to oven hardening at 130°C for 480 hrs (**Fig.**
206 **3(b)**). The patterns generated from the two methods demonstrate that the sulfoxide index gives
207 an effective way to describe the OH in EBs.

208 The viscoelasticity behaviour is determined by exploring the frequency-dependent
209 material properties (i.e., complex shear modulus and phase angle) of the binders. Due to the
210 fact that EBs consist of a wide range of temperature-dependent molecular structures with
211 various polarities, the viscoelasticity of these binders is related completely on the interactions
212 between the different structures and their chemistry.

213 **Fig. 4** shows the complex modulus master curves for the binders after oven hardening at
214 130°C. These curves demonstrated the influence of OH on the viscoelastic behaviour of the
215 different EBs. It can be observed that the complex modulus increases slowly over the first 24
216 hrs of hardening, in which the network formation has been formed and the material hardens
217 due to curing, and then increases substantially as time increases up to 480 hrs. At relatively
218 low frequencies, the complex modulus increases continuously at all time lengths. The
219 modulus tends to merge together to the same value at higher frequencies for both EB20 and
220 EB50. The performance is clearly dominated by the inclusion of epoxy modifier into the
221 bitumen. The slight difference between the modulus at EB20 and EB50 is due to that fact that
222 epoxy molecules need more time to link with each other at low modification levels.

223 The phase angle master curves are not as straight forward as the complex modulus
224 mastercurves and the epoxy modifications in the bitumen showed considerable reductions in
225 phase angle. The phase angle is measured of the time lag between an applied stress and the
226 resulting strain and indicates whether a binder will behave as elastic-, visco-elastic or
227 viscous-dominated material. When the phase angle is low, the material is more elastic. For
228 EB20 and EB50, it can be seen that the modulus is higher at longer hardening times but the
229 slope of the phase angle of EB50 is different than of EB20. From the results it can be seen
230 also that the modifier had insignificant effects on the phase angle at relatively low
231 frequencies. The presence of phase angle plateaus at intermediate frequencies for EBs
232 indicates the epoxy molecular networks in binders. The modifier enhanced the elasticity of
233 bituminous material. The material behaves more glassy when the hardening process has been

234 completed, due to the dominance of modifier in EB50. Measurements of phase angle are
235 more sensitive to chemical changes and thus the modification of bitumen than modulus.

236 The above findings have suggested that it could be interesting to link the evolution of
237 viscoelastic properties to the chemical characteristics of the binders during OH. **Fig. 5(a)** and
238 **Fig. 5(b)** show the relationship between the sulfoxide index and the changes in complex
239 modulus and phase angle at 10 Hz, respectively, indicating a linear relationship for all binders
240 over the OH extent. This performance indicates that the sulfoxide formation tends to correlate
241 with increased modulus and reduced phase angle as the binders harden. In addition to this
242 observation, the viscoelastic response of binders subjected to PAV hardening provided almost
243 identical hardening with the oven hardening for 480hrs, with the EB50 and EB0 showing the
244 highest modulus and lowest phase angle, respectively. Finally, since the level of OH is of
245 primary concern when comparing hardened binders, it is reasonable to conclude that addition
246 of epoxy modifier generates more resistant binders against oxidative aging. However, the
247 lower the phase angle at the same stiffness, probably the more susceptible a binder becomes
248 to monotonic and cyclic fracture. For this reason, the tensile strength characteristics and the
249 fatigue life of studied binders were assessed as well, and the results are given in a later sub-
250 section.

251

252 **Chemical controlled Hardening**

253 According to the previous observation (see **Fig. 2(a)**), the initial fluctuation of carbonyl indices
254 at the beginning of hardening (from 0 to 8 hrs) may be related with the possible contribution
255 of these compounds to CH. For this reason, the time between 0 to 8 hrs is assumed to be the
256 time window for CH.

257 **Fig. 6(a)** demonstrates that the intensity of oxirane reduces with prolonged hardening time
258 for both EBs tending to converge as time increases. The epoxide rings (C_2H_4O) are opening
259 through the consumption of oxirane and new compounds are formed. The hardener is
260 considered to be an acid-type since the carbonyl acid group decreased over time similarly
261 with the oxirane group. This performance indicates that the carbonyl acid and oxirane
262 precursors (the reactive groups) were consumed almost completely after approximately 5 hrs
263 at 130°C. Ester ($RCOOR'$) and ether (ROR') compounds increase initially while remaining
264 constant after a time period indicating that esterification and etherification reactions take
265 place during the CH. Therefore, it is assumed that oxirane and carbonyl acid groups reacted
266 together to create the crosslinked network into the bituminous phase and formed the ester and
267 ether groups (**Fig. 6(b)**). Moreover, the level of epoxy modification affects the CH
268 accelerating the reactions when higher epoxy amounts were used. The network of epoxy
269 modifier (as resulted from the polymerization of epoxy resin in part A of modifier with the
270 assistance of hydroxyl functionalities of hardener in part B) is formed slightly faster when
271 higher modification levels are applied, mainly because there is less bitumen available to
272 prevent the network evolution. Moreover, it can be seen that longer hardening times produces
273 a higher curing increment. This can be seen from the steeper curve shape at the higher
274 modification level (EB50) than at a lower (EB20).

275 FTIR spectrometer, MDSC and DSR analyses were conducted to explore the increase of
276 T_g and modulus of crosslinking epoxy binders within the CH window. As shown in **Fig. 7**,
277 the presence of the epoxy modifier in the bitumen causes an increase of modulus and T_g
278 whereas longer hardening times also increase both parameters. On the one hand, the increase
279 of mechanical and physical parameters as depicted in **Fig. 7** is related to the increase of
280 crosslinking density until a point that represents the ultimate value corresponding to the
281 completion of CH. Also, these results show that both material parameters are very sensitive to
282 small changes in the microstructure of bitumen at a constant (high) temperature, and
283 consequently of the crosslinking network of the reacting modifier.

284 On the other hand and from the molecular viewpoint, bitumen consists of a plethora of
285 molecules classified into asphaltene and maltene fractions. Asphaltenes (polar compounds)
286 are dissolved into the maltenes medium of various in terms of polarity compounds. In
287 addition to the fact that at very low temperatures, the T_g of bitumen correlates mainly to the
288 non-polar compounds of maltene medium (T_g) (26), the polar epoxy chains-asphaltene
289 interactions could result increase of mobility of non-polar moieties leading to T_g decrease.
290 However, from **Fig. 7**, the T_g increases over time during CH showing that the bitumen almost
291 does not participate and the epoxy-asphaltene interaction is limited in CH. It is assumed that
292 bitumen reduces the contact opportunities between unreacted parts of modifier still available
293 in the matrix and hence EBs release less heat. In other words, bitumen inhibited the
294 polymerization reactions between the two epoxy parts leading to reduction of maltenes
295 mobility and subsequently to T_g increase. In general, differences in polymer crosslinking
296 structures in fully hardened modified binders are related also to the polarization and
297 orientation of reacted molecules and the reaction pathways.

298

299 **Mechanical Performance of CH Hardened Binders**

300 The tensile characteristics of fully chemically hardened samples (i.e., at 130°C after 5 hrs)
301 under monotonic direct tensile load was examined as well. In general, the tensile strength of
302 the samples depends on the extent of the hardening reaction, the ratio of the unlinked
303 molecules to crosslinked molecules and the internal chemical structures. The modified
304 binders experienced ductile behavior, and thus exhibited higher flexibility characteristics than
305 the base bitumen (**Fig. 8(a)**). Modifier enhances greater toughness in the bituminous system
306 forming materials of high tensile failure resistance (i.e., high tensile strength), and this
307 strength increased with the content of modifier into the bitumen (**Fig. 8(b)**).

308 Finally, the fully hardened samples (i.e., at 130°C after 5 hrs) were exposed to cyclic
309 loading at three different shear stress levels in the DSR to assess the fatigue properties of
310 these newly developed binders. As shown in **Fig. 9**, the fatigue life at all three stress levels is
311 higher for the epoxy modified binders than for the unmodified bitumen (EB0). The difference
312 at lower stress levels is huge. In conclusion, not only the toughness of the modified
313 bituminous also improved the fatigue performance. Combination of these properties with low
314 temperature behaviour can strongly increase cracking resistance at all temperatures.

315

316 **SUMMARY AND CONCLUSIONS**

317 In this paper, epoxy polymerization-induced physiochemical phenomena have been related to
318 the mechanical properties, and two corollaries to the chemical analysis were made helping to
319 understand the behaviour of EBs. Firstly, the increase and the decrease of certain carbonyl
320 compounds (increase of carbonyl ether and ester, decrease of carbonyl acid) at the beginning
321 of hardening (i.e., the first 5 hrs) indicate that the esterification and etherification (CH) are
322 taking place due to the reaction of hardener (part B of modifier) with the epoxy resin (part A
323 of modifier). Second, the inconsistency of carbonyls for the short and long time intervals in
324 the oven- and PAV-hardening leads to the conclusion of termination of chemical and the
325 initiation of age hardening after 5 hrs, respectively. The sulfoxide index is proposed to be an
326 efficient indicator for evaluating the aging extent of epoxy modified binders. With regards the
327 mechanical performance of EBs, the complex modulus of EBs is similar to base bitumen, and
328 EBs provide higher tensile strength, flexibility and enhanced fatigue performance.

329

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335

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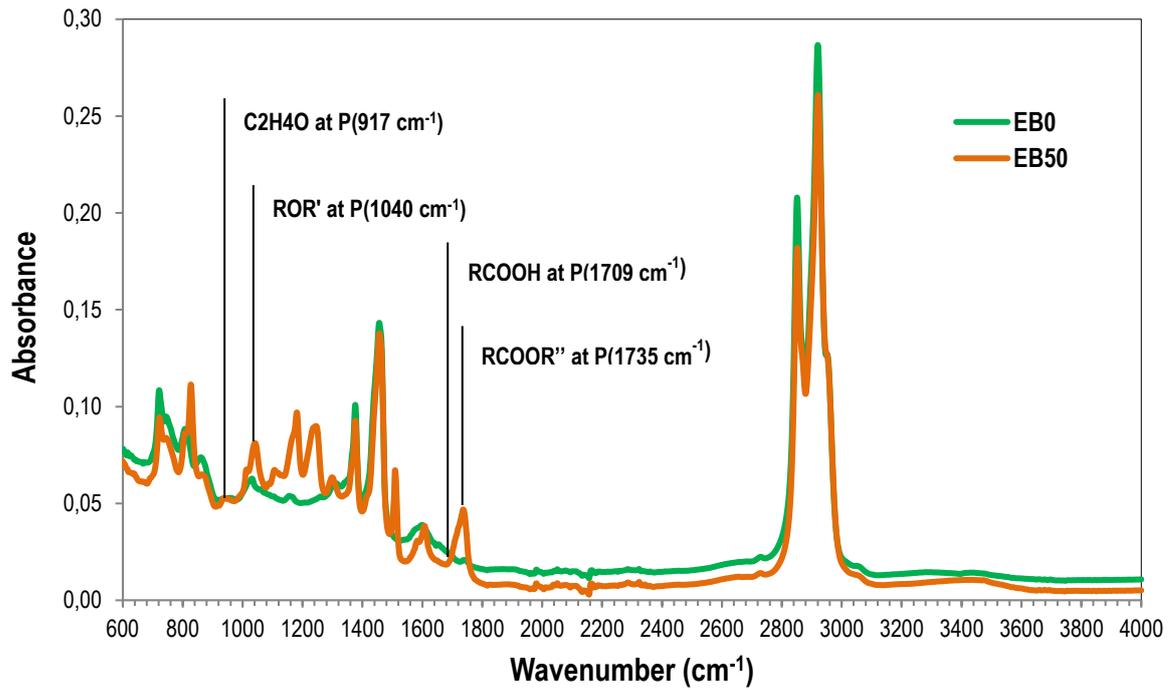
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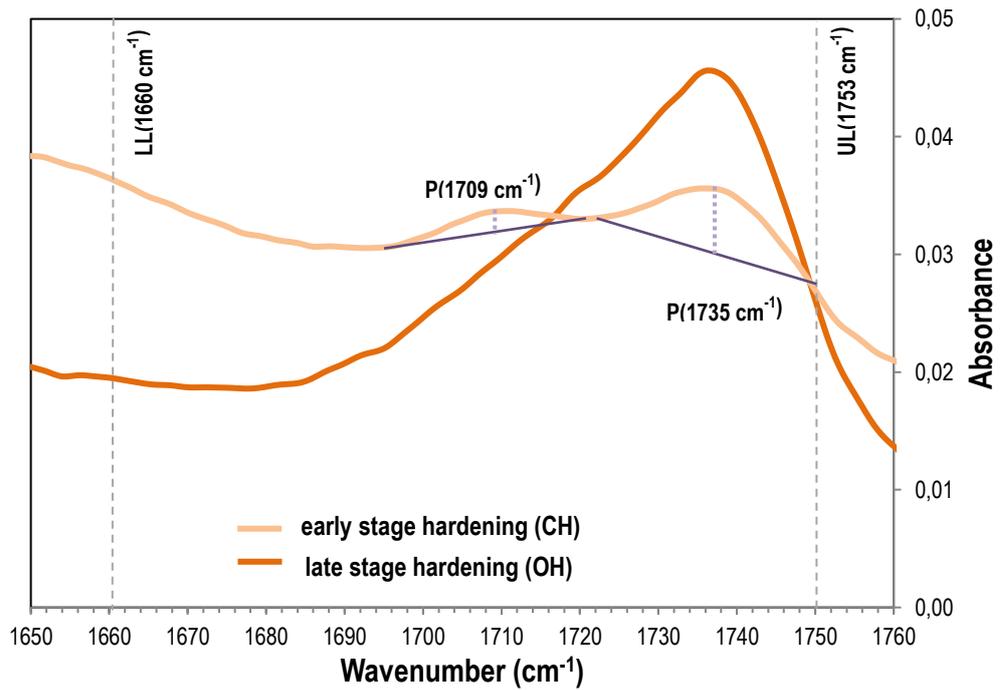
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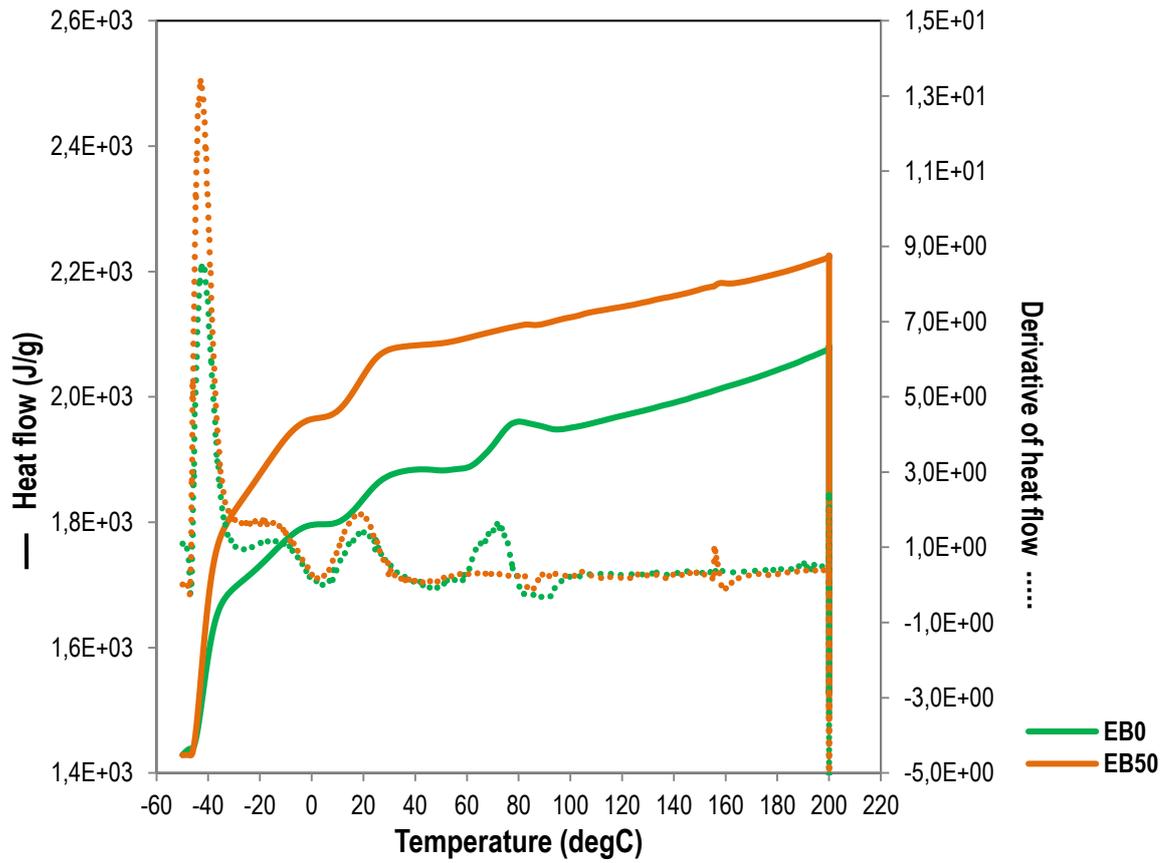
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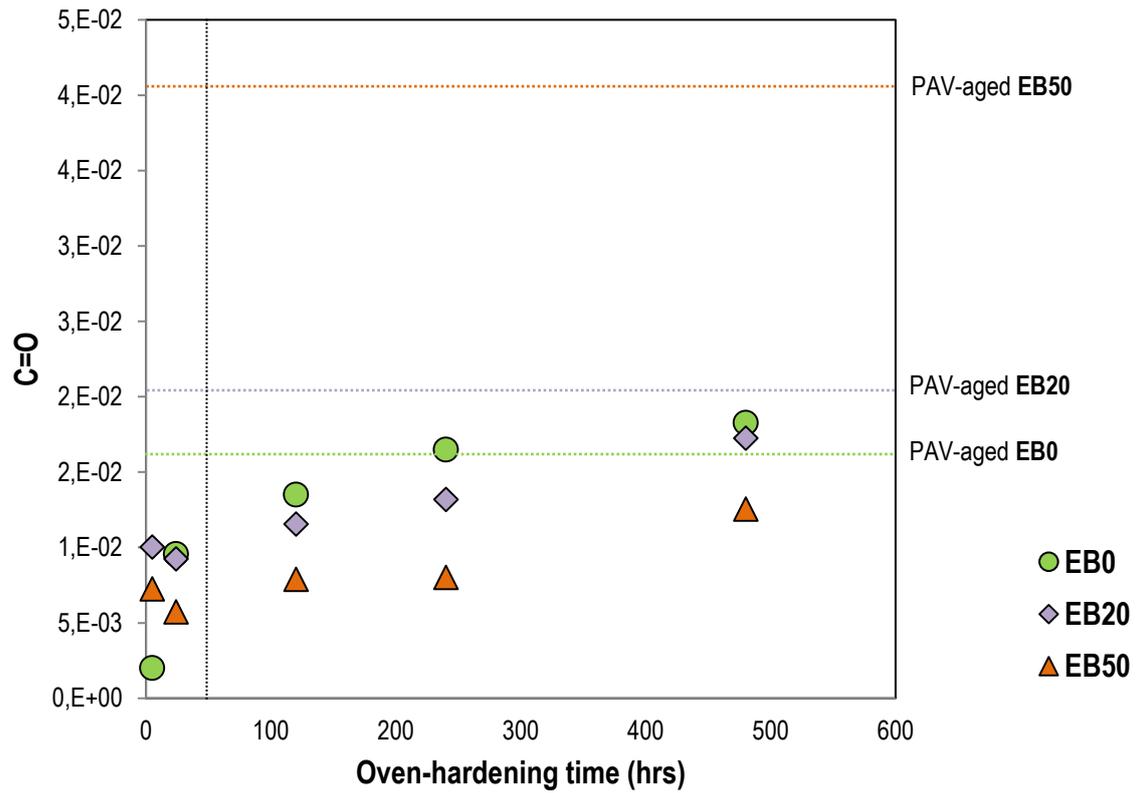
(b)

FIGURE 1 FTIR spectra of (a) base and epoxy modified bitumen (EB50) at late hardening stage, and (b) band area and peak values and limits for carbonyl groups of EB50 at an early and a late hardening stage



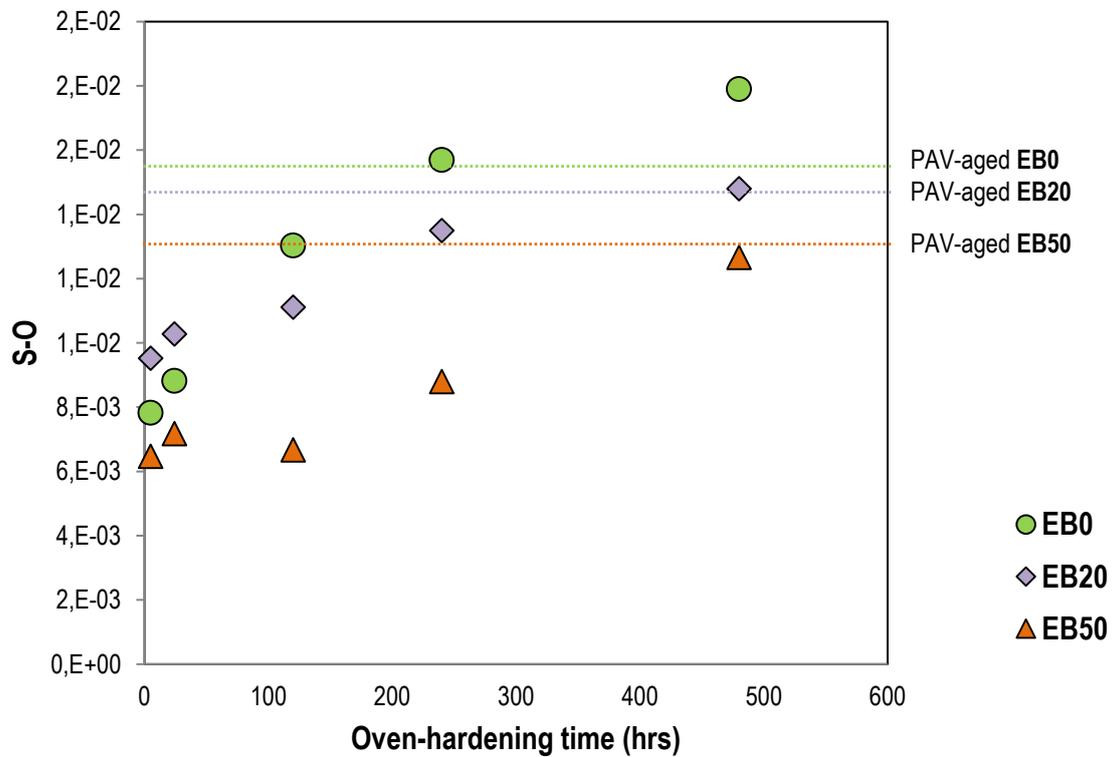
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FIGURE 2 MDSC scans at 40°C/min from -50 to 200°C of base and epoxy modified bitumen (EB50)



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(a)

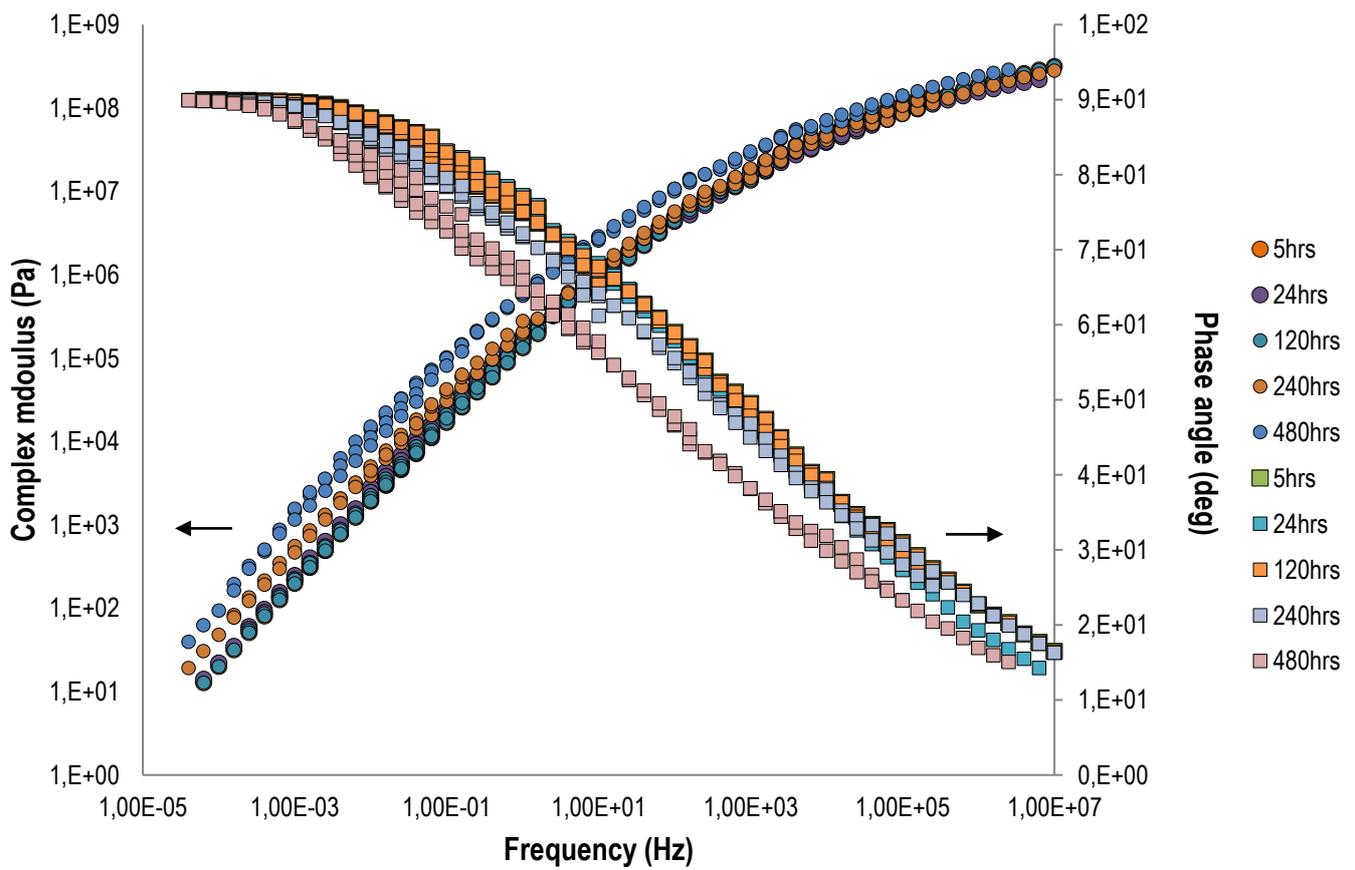


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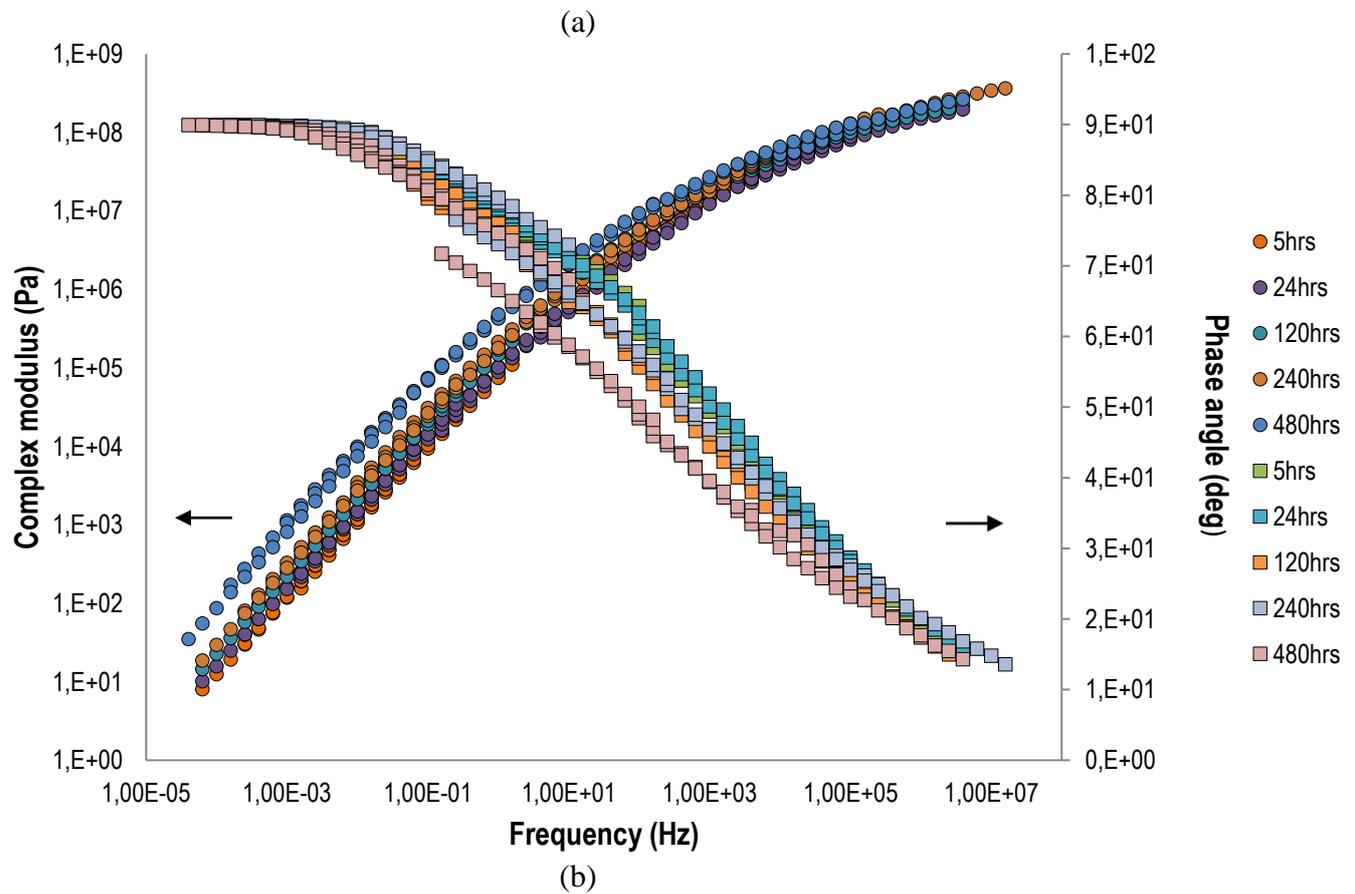
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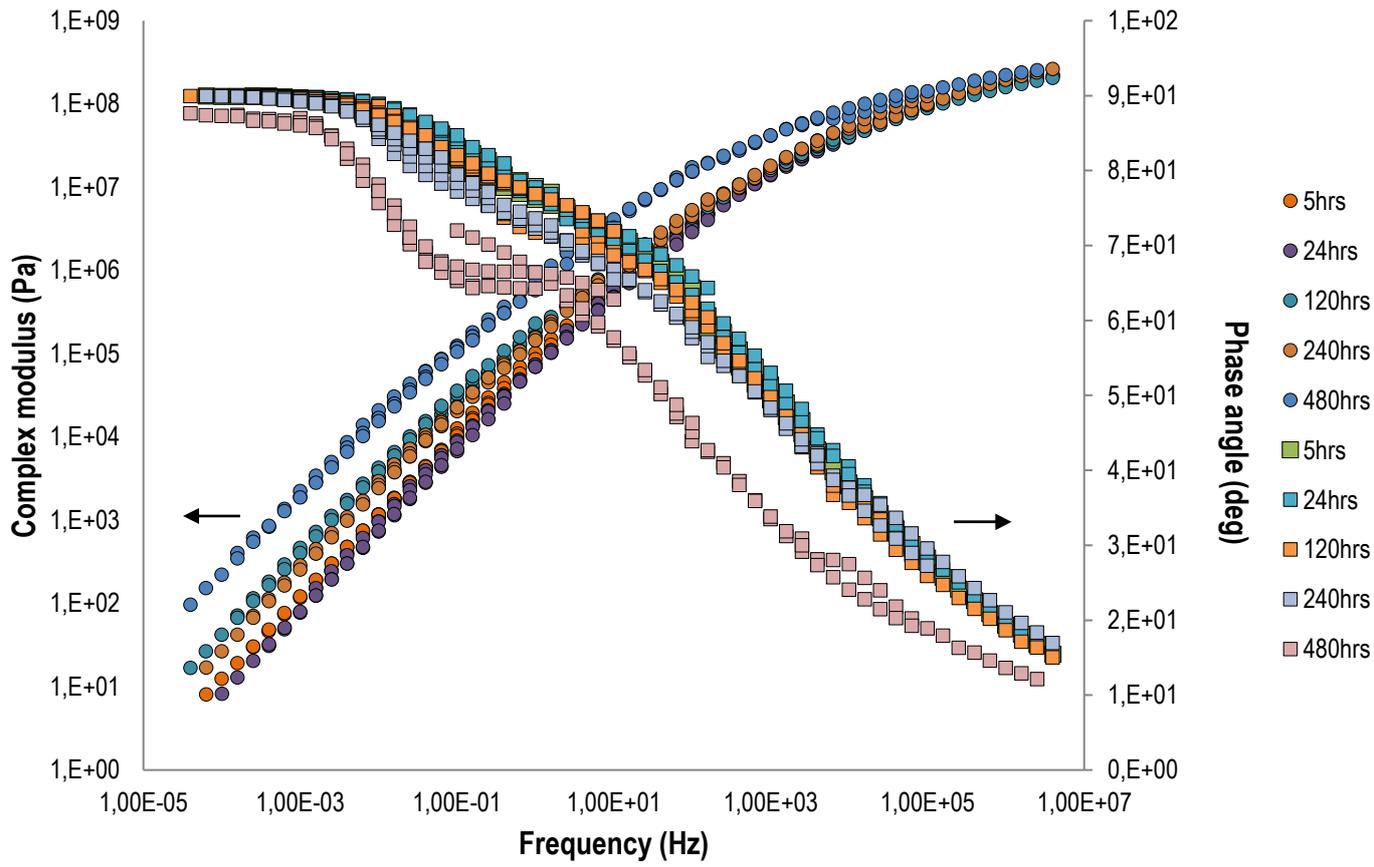
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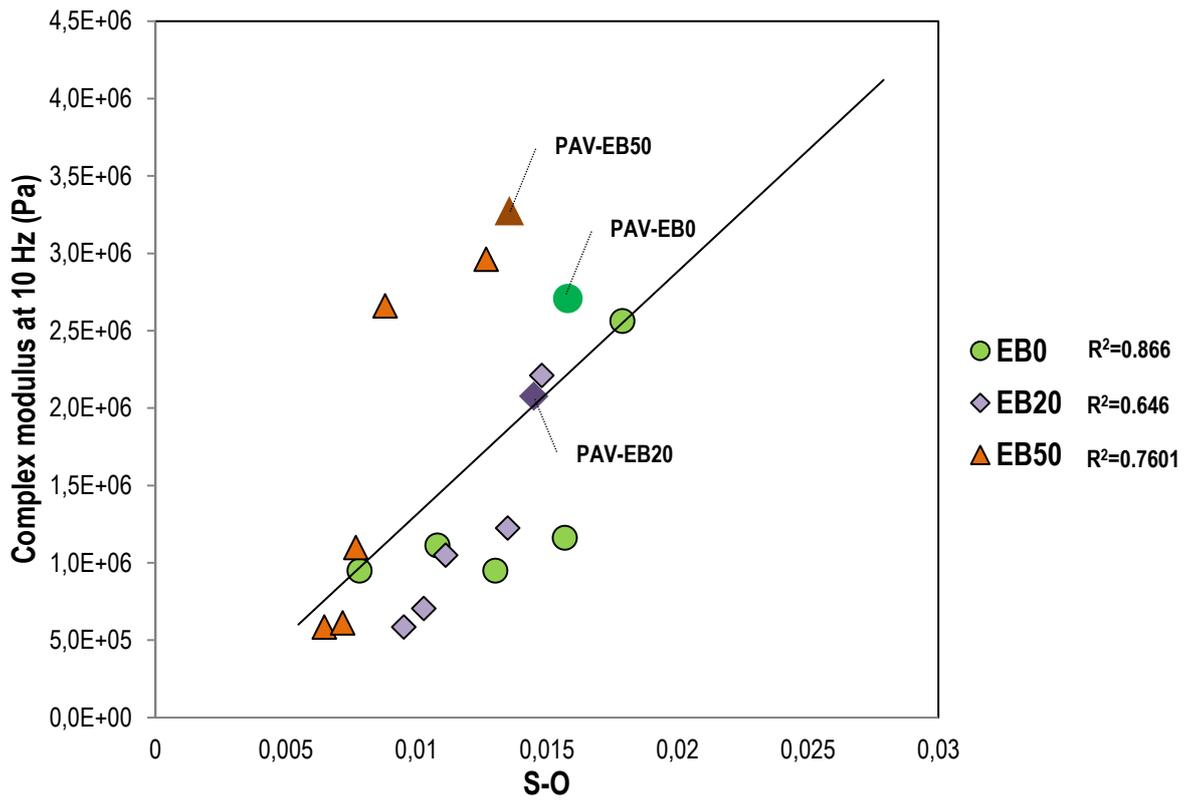
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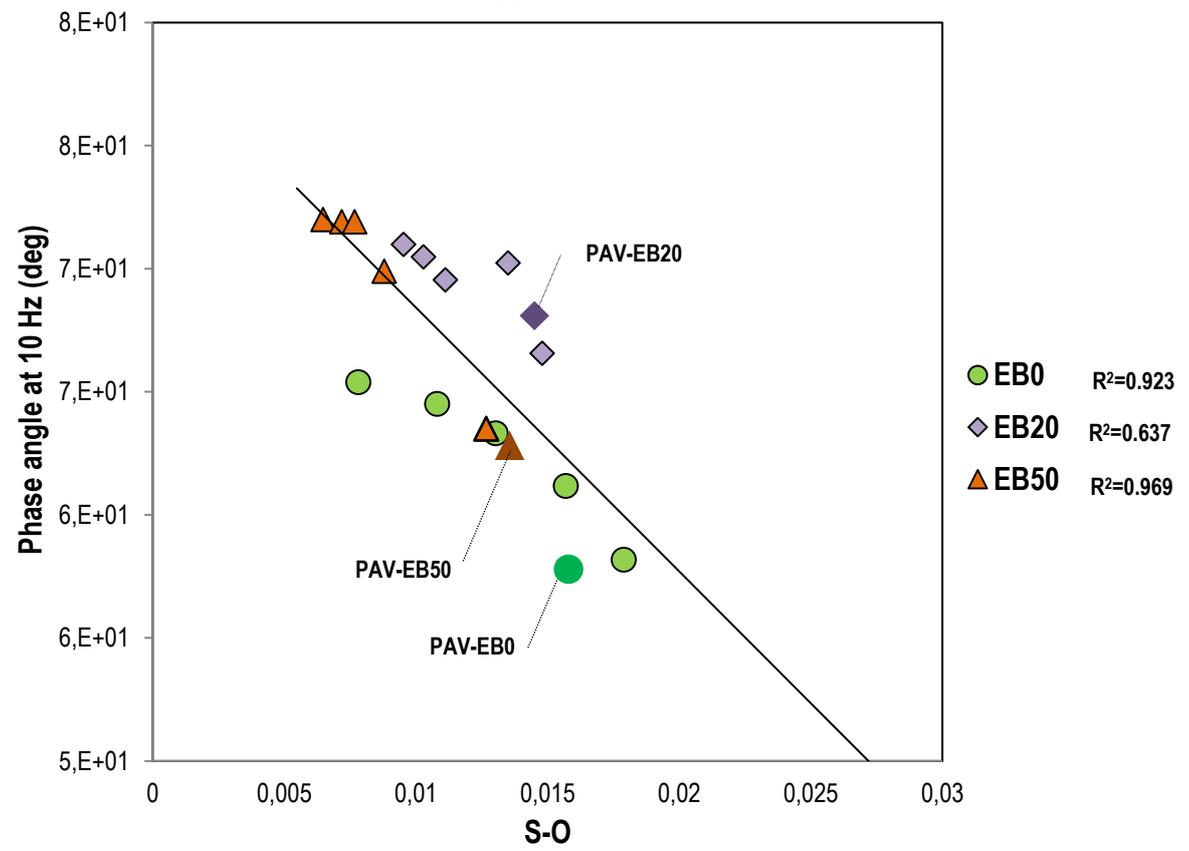
(c)

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FIGURE 4 Master curves of complex modulus and phase angle of studied binders after OH for different times; (a) EB0, (b) EB20, and (c) EB50

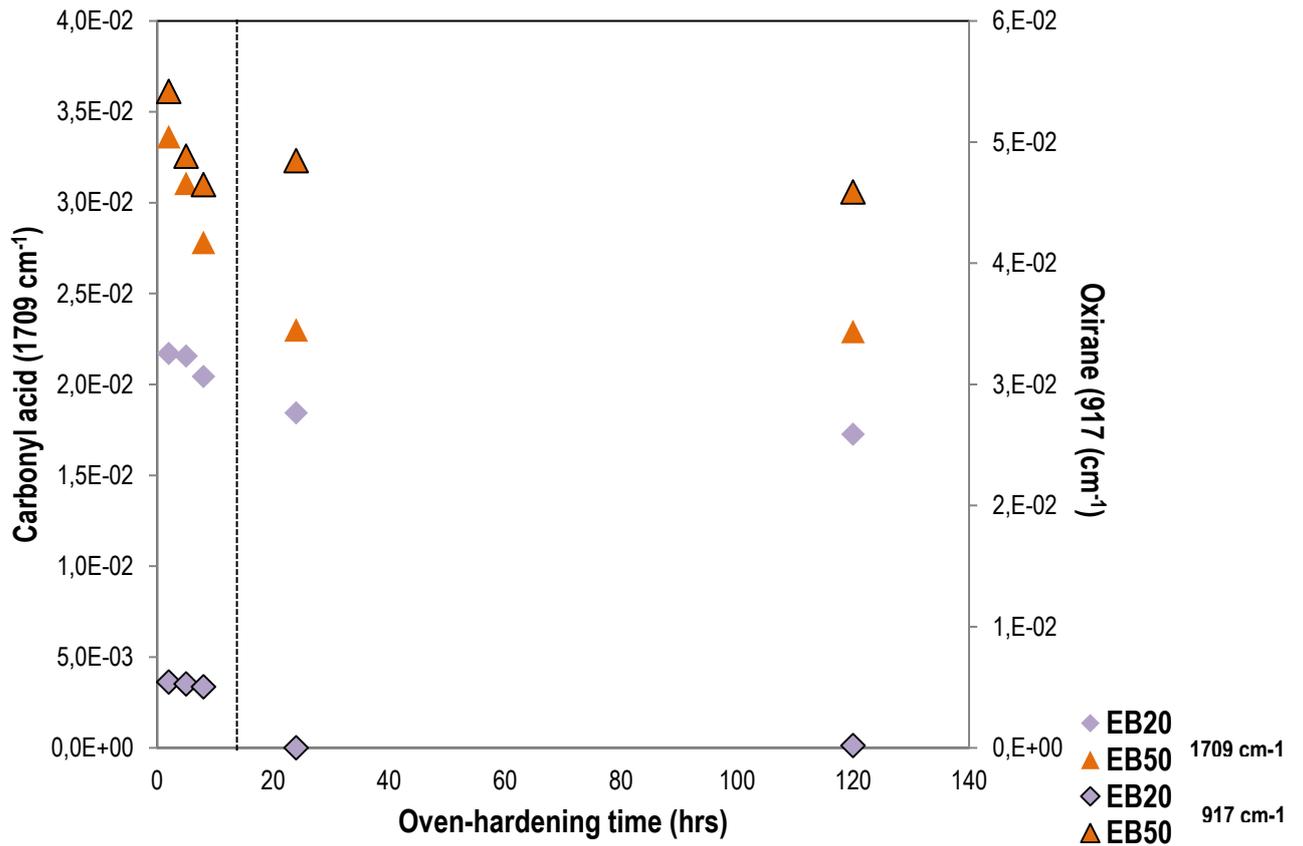


(a)



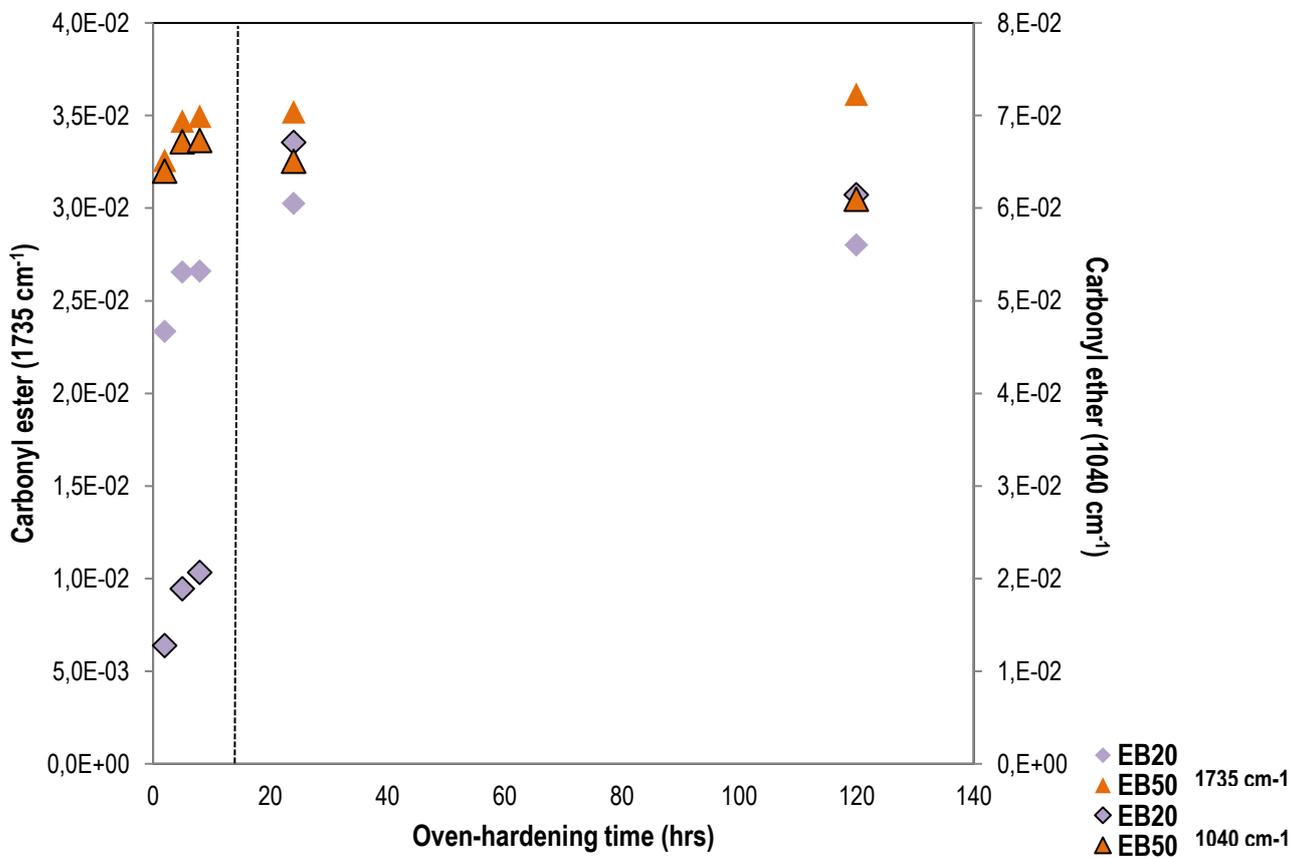
(b)

FIGURE 5 Relationship between sulfoxide compounds and viscoelastic properties over OH hardening: (a) complex modulus and (b) phase angle



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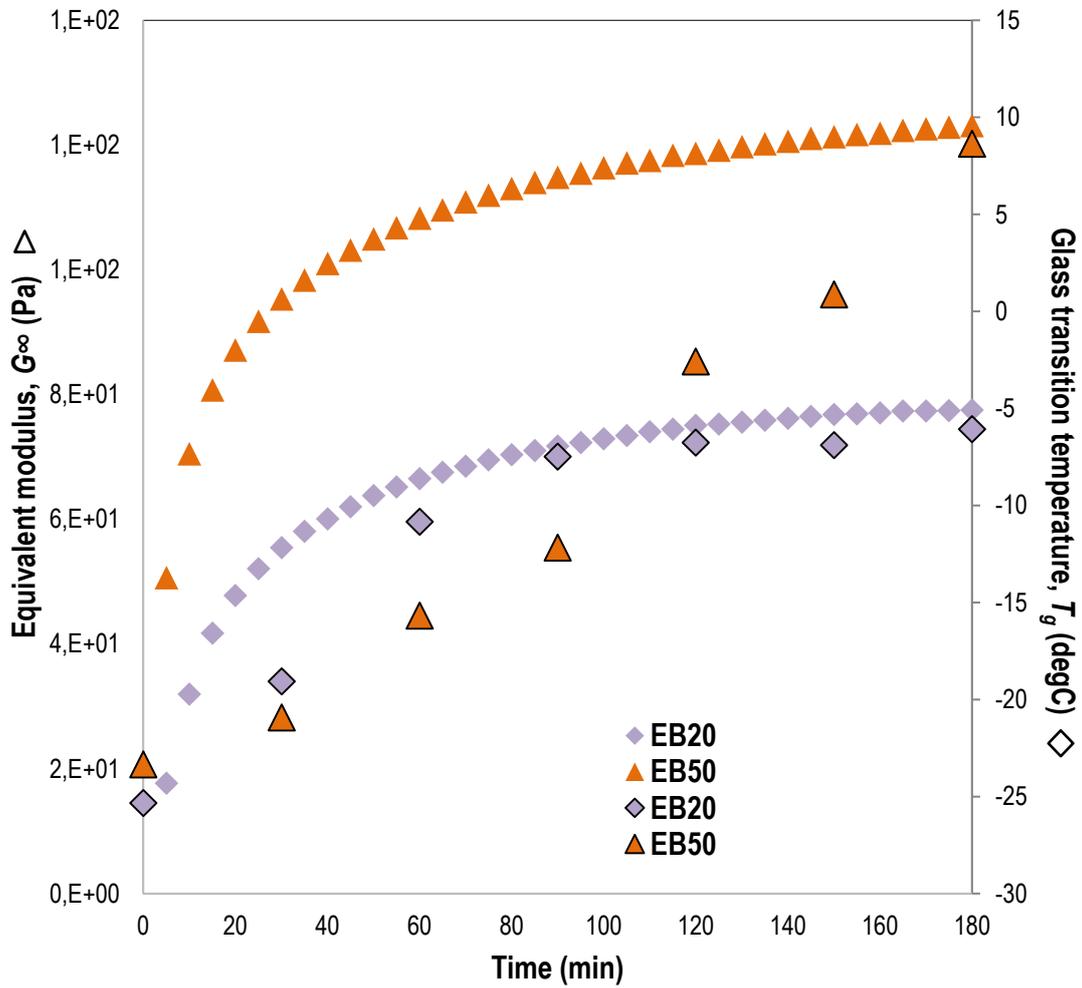
(a)



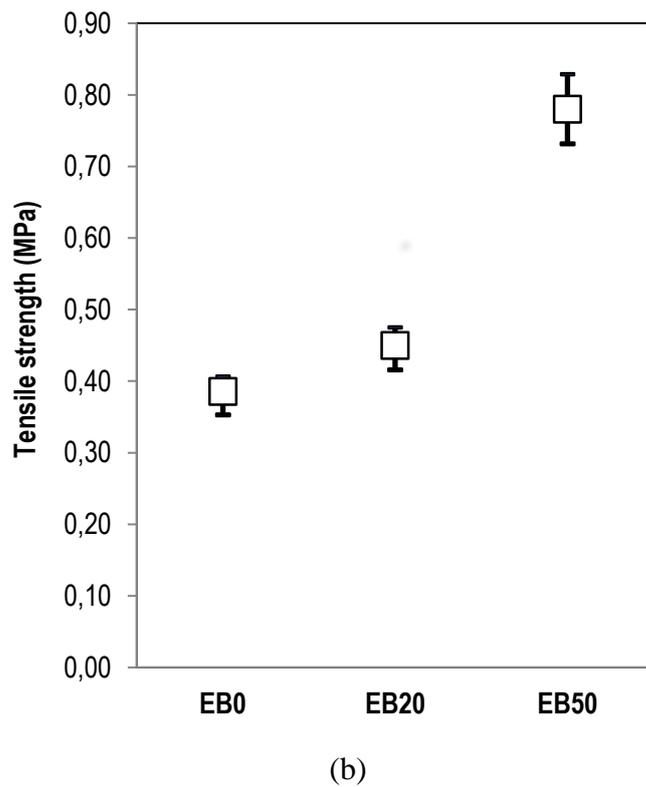
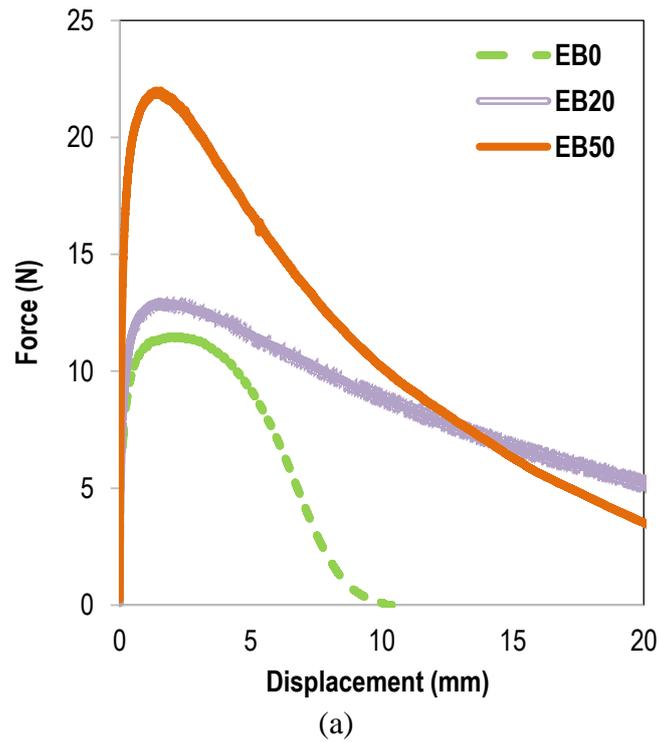
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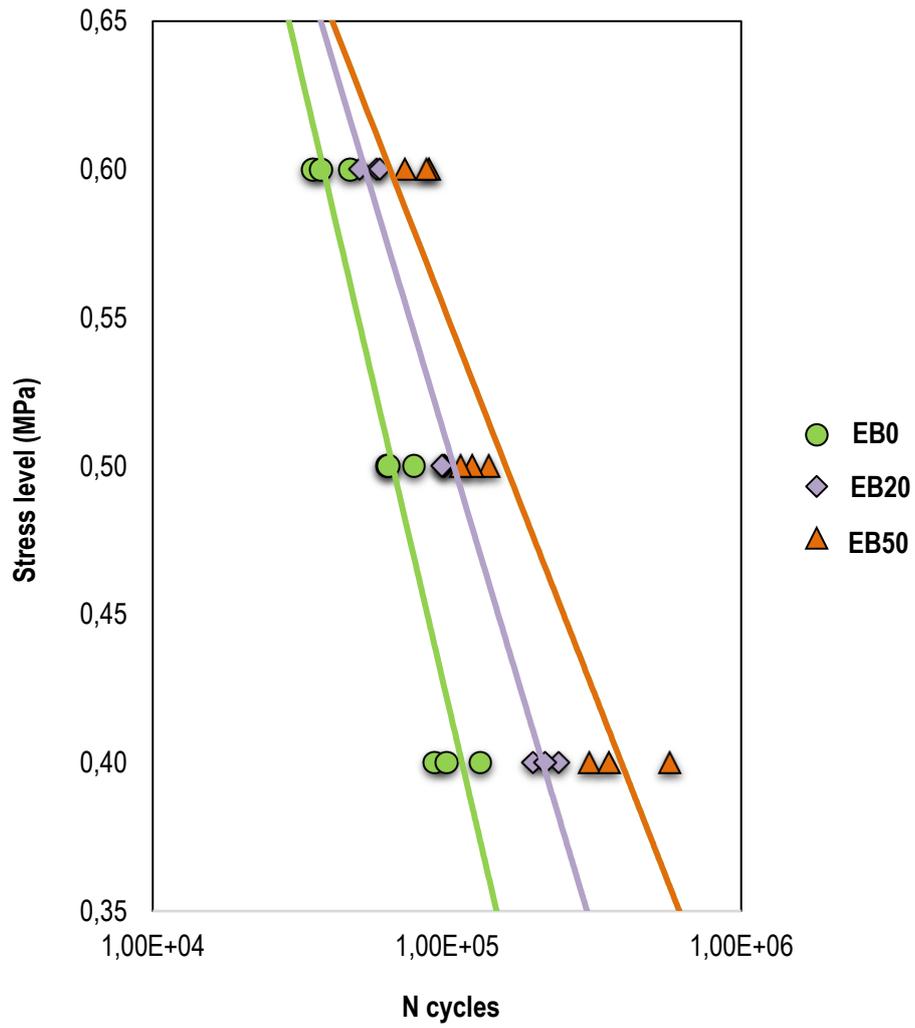


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