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Chemo-rheological Study of Hardening of Epoxy Modified Bituminous Binders with the Finite Element Method

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38 **ABSTRACT**

39 The chemical irreversible hardening of epoxy modified bitumen is affected by various
40 physical factors and the successful application of this technology is directly linked with full
41 understanding of chemo-rheological material characteristics. This study proposes a model to
42 describe the material viscosity evolution during hardening of epoxy modified bitumen. The
43 findings from numerical analyses performed to assess the mechanical response of epoxy
44 modified bituminous binders are presented. Information of the chemical interaction of epoxy
45 within a bituminous matrix was collected and all the influential factors have been determined.
46 The proposed chemo-rheological model accounting for the polymerization of the epoxy in the
47 bitumen was formulated and the sensitivity of material parameters, such as activation energy,
48 reaction order and extent of hardening reaction until the gel point of epoxy modified binders,
49 was demonstrated. Results of the analyses suggest that lower levels of activation energy
50 increase the degree of hardening and the rate of viscosity development. By decreasing the
51 hardening reaction until the gel point the achieved viscosity of epoxy modified bitumen was
52 increased showing the importance of gel reaction extent on material viscosity evolution. The
53 numerical studies have shown also that the polymerization rate in the epoxy modified
54 bitumen is highly dependent on the temperature under various (non-) isothermal conditions.
55 Also, the polymerization rate should be considered through all the material curing processes
56 to avoid unwanted variations in the mechanical properties.

57

58 **INTRODUCTION**

59 Due to the challenge to minimize the public expenditures and the road administration costs
60 for repairing and re-paving the transport infrastructure networks, epoxy modified bituminous
61 binders have captured the interest of road authorities as an important alternative to
62 conventional binder technologies. Nowadays, bituminous materials modified with epoxy-type
63 resins are used mainly for pavements in tunnels, steel deck bridges and at intersections of
64 heavy duty roads to provide enhanced performance without major repairs for more than 30 to
65 40 years (1-5).

66 Recent studies suggest a successful industrial transfer of this technology to pavements but
67 contractors still face serious issues during mixing, transport and pavement construction
68 phase. Two main issues are for example the accelerated and the slow chemical hardening of
69 material before compaction and during the early traffic period, respectively (6). Moreover,
70 production plants need to be modified to allow proportional in-line feeding of epoxy
71 modifiers into the pugmill (i.e., through a static mixer before adding them to the drum). The
72 chemical reaction rate of epoxy with the bituminous phase is influenced by several factors
73 such as the added hardening agents, the working temperature, mixing time in-plant, transport
74 and compaction of the mix on the road. Higher mixing temperatures accelerate the hardening
75 reactions of epoxies in bituminous mixes and lower the time window for material transport
76 and compaction. As a consequence of the above, it becomes obvious that it is crucial to have
77 full control over the whole production chain of epoxy modified pavement structures.

78 In comparison with bituminous mixes, the processing of epoxies and epoxy modified
79 bituminous composites is more complicated and more difficult to control because of the
80 chemical reactions that take place. The chemical hardening of epoxy modified bitumen due to
81 crosslinking of linear prepolymers and the polymeric network formation from monomers is a
82 complex process that involves the continuous chemical alteration and interaction of epoxy
83 resin with the bituminous binder. Within this framework, the development of rheological
84 properties plays an important role to characterize the mix workability and performance before
85 and after construction. To optimize the processing and the properties of the epoxy-bituminous
86 materials it is necessary to understand the chemo-rheological relationship which varies at
87 different temperatures and time as polymerization reactions proceed.

88 This study proposes a chemo-rheological numerical model able to describe the mechanical
89 response of epoxy modified bituminous binder during material chemical hardening. The
90 proposed chemo-rheological modelling approach accounting for the epoxy polymerization
91 within the bituminous matrix and the sensitivity of the physical model parameters on the
92 mechanical response of the matrix were investigated by performing numerical analyses.

93

94 **EPOXY MODIFIED BITUMINOUS BINDERS**

95 Bituminous binders are characterized by their high chemical complexity containing various
96 molecular types. Bitumen is mostly classified based on differences in their solubility and
97 polarity into two major groups; asphaltenes and maltenes. The fraction of asphaltenes
98 consists of highly condensed planar and heteroatom polar groups, polar aromatic rings and
99 large amounts of heteroatom polar functional groups. The maltenes fraction is sub-divided in
100 saturates, aromatics and resins groups (7). On the other hand, the epoxy-type systems are
101 copolymers which consist typically of two liquid components, the monomers or short chain
102 prepolymers with epoxide groups at their ends named epoxy resins and the co-monomers
103 which react with the epoxides named hardening agents. These two components are combined
104 and crosslinking chains of molecules are formed through the polymerization process. When
105 these components are mixed with bituminous binders they produce paving materials with
106 enhanced durability and increased longevity.

107

Epoxy Resins Incorporation into Bituminous Binders

Initially, epoxy resins were added in bituminous binders to minimize the thermal susceptibility and permanent deformation of asphalt concrete mixes since the thermoset nature of epoxies results in excellent rut resistant binders. Later on, it was realized that the polymeric structure of epoxy within the bituminous matrix enhanced the fatigue, moisture and oxidative degradation resistance of bituminous mixes (1-6). These materials cannot be re-melted and their application in pavements has been predominantly for high-performance solutions which does not need any special construction equipment.

However, epoxy modified bituminous binders are thermo-dynamically immiscible blends appearing phase separation issues, mainly at elevated temperatures. Experimental observations showed that, in the epoxy modified bitumen, part of the binder is substituted with epoxy and an archipelagos of polymeric chains is dispersed in the continuous bituminous rich phase as polymerization proceeds. The structure of these chain networks dramatically influences the hardening crosslinking density, the characteristics of crosslinking chains (i.e., the size) and, consequently, the final product properties. For the material preparation, rapid epoxy-bitumen blending and addition of extra compatibility agent can assist on producing homogeneous thermoset dispersion in toughening bituminous blends. The most preferred is formed by epichlorhydrin and bisphenol A-based epoxy resin (2, 4, 6) which needs a mixing temperature of 110-120 °C and a time available of 57-94 minutes transported from the production plant to field (6).

Hardening Agents Incorporation into Bituminous Binders

Typically, the hardening agents react with the epoxide groups of resins to produce covalent bonds. Based on the type of hardening agent used, the epoxies are classified as amine- and acid-type resins. The application of epoxy resins is a well-established field in several industries and the performance of epoxy-hardening agents is extensively studied. For pure epoxies, acid anhydrides are preferred above the organic acids, which are less soluble in resins and sometimes release water during the polymerization process. Also, acid anhydrides are more often applied in epoxies than the traditional amine-based agents since they provide higher compatibility and better thermal stability with epoxies, leading to a rapid viscosity reduction when mixed (8, 9).

In the paving industry, acids and anhydride acids are commonly used with a typical completed reaction after 4h at 120 °C. It is reported in the literature that methyl tetrahydrophthalic of cyclic molecular structure, methyl hexahydrophthalic and tung oil anhydrides improve the compatibility of bitumen and epoxy. They help to produce materials with enhanced strength and heat resistance (10-12). However, the high volume of rigid benzene groups in epoxy-methyl tetrahydrophthalic system could limit its applicability. Polymerized fatty acid agents have been synthesized successfully and added to the system together with tung oil maleic tribasic acid agent to increase the stability between the components (13). Moreover, stable modified binders of short polymeric chains are produced when epoxy modified bitumen is hardened with maleated bituminous agents (14).

Also, amine-type hardeners have been used for epoxy-bitumen blends. For example, octadecylamine, an aliphatic amine, has shown a very quick hardening effect (1h at 150 °C or 3d at 60 °C) but resulted in an unstable epoxy-bitumen with restrictions for the amount of bituminous binder to be used (15). This had direct effect on the total cost since the limited relative volume ratio of the bitumen causes not only a more expensive but also a less viscoelastic material. On the other hand, a polyetheramine was used with longer chains and polar ether groups to increase the stability between epoxy and bitumen without phase separation and to provide an inexpensive hardening option with sufficient hardening rates (1h at 160 °C or 3d at 60 °C) for paving applications (16). It is believed that the performance of

158 this hardener is related to the light crosslinked networks formed within the bituminous
159 matrix.

160

161 **MOTIVATION AND OBJECTIVES**

162 In contrast to the wax fraction and the crystallization related physical thermo-reversible
163 hardening in pure bituminous binders (17, 18), the chemical irreversible hardening of epoxy
164 bituminous materials is influenced by different factors. Apart from the influence of
165 isothermal conditioning on material stiffening for both physical and chemical hardening, the
166 evaluation of reaction order, frequency and activation energy of hardening is of great
167 importance to predict the hardening phenomena and to reach optimal cure. Therefore, an
168 appropriate chemo-rheological model which can describe the reaction processes to avoid
169 unwanted variations in the mechanical properties (i.e., complex modulus, phase angle,
170 viscosity) of epoxy modified bituminous binders is required. The model should be capable of
171 simulating not only the temperature-time process of various operations but also the influence
172 of different resins, agents and other additives on properties to design a better material.

173 The objective of this study is to introduce a procedure to predict the hardening of epoxy
174 modified binders by taking into account their time-temperature dependency. Also, the
175 proposed procedure can be used as a tool to understand the chemical hardening of blend and
176 to calculate the mechanical properties of epoxy modified bitumen throughout the
177 polymerization reactions phase. Since it is crucial to identify the influential parameters of the
178 processes, the model has been deployed to simulate the reaction temperatures and the
179 chemical conversion of these materials.

180

181 **MODELING OF EPOXY MODIFIED BITUMEN HARDENING**

182 Extensive researches (19-22) have been conducted to develop models for describing the
183 chemo-rheological behavior of epoxies with the phenomenological model rather than a
184 mechanistic one when the hardening process is very complex. Among others, the
185 autocatalytic models have been successfully applied to various thermosets. Also, models
186 developed based on n -th order kinetics can describe sufficiently the chemical hardening of
187 modified thermoplastic blends of relatively low amount of thermosets (23, 24). Since
188 previous investigations have shown no significant effect on the extent of the epoxy hardening
189 after blended with bitumen under the same conditions (16), the exothermic reaction is
190 considered as an one-step n -th order reaction with negligible secondary reactions in this
191 study.

192 The exothermic polymerization reaction rate of an epoxy-bitumen blend is a temperature
193 dependent reaction and the conversion is initiated via heating. Hence, the ability of the epoxy
194 modified bitumen to harden at a sufficient time depends on the temperature of initial blending
195 in-plant production, material transport, laying and compaction. To simulate the reaction, the
196 heat transfer and the viscosity evolution mechanisms of the complex chemical hardening
197 processes of epoxy modified bituminous binders, the governing equations are given in the
198 following sub-sections.

199

200 **Governing Hardening Kinetics Equation**

201 In polymerization process of epoxy modified bitumen, the kinetic model allows to predict
202 the chemical conversion or hardening degree α and the reaction rate as a function of time
203 and temperature as follows :

204

$$\frac{\partial \alpha}{\partial t} = K(T) \cdot f(\alpha) \quad (1)$$

205

206 where $K(T)$ is a temperature-dependent parameter, which is described by an Arrhenius
 207 equation, and $f(\alpha)$ is a function of conversion. Also, the shape of the $f(\alpha)$ shows the reaction
 208 performance of system and is determined by the n -th order kinetics.

209 Therefore, the rate of change of hardening degree is described as :

210

$$\frac{\partial \alpha}{\partial t} = k_0 \exp\left(-\frac{E_a}{RT}\right) \cdot (1 - \alpha)^n \quad (2)$$

211

212 where k_0 is the pre-exponential kinetic factor, E_a is the activation energy or the energy
 213 barrier to be overtaken to begin the reaction, R is the universal gas constant and n is the
 214 reaction order upon the hardening mechanism.

215 During chemical hardening of pure epoxies under isothermal conditions, the total cure of
 216 the resin is not always achieved, due to the fact that the glass transition temperature of epoxy
 217 increases progressively during hardening. The crosslinked molecules do not flow easily when
 218 the conditioning temperature of epoxy becomes the full polymerization temperature and,
 219 thus, their mobility lowers. Therefore, the Eq. 2 is not always valid for modelling the epoxy
 220 resins. However, in the case of epoxy modified bituminous mixes, it is assumed to be a
 221 sufficient function for describing the chemical reactions of these materials. An illustration of
 222 crosslinked molecules of epoxy within the bituminous matrix is given in **Fig. 1(a)**.

223

224 **Governing Heat Transfer Equations**

225 The governing equation of the transient heat conduction within the epoxy modified bitumen
 226 is described by :

227

$$\rho c_p \nabla T - \nabla \cdot (k \nabla T) = Q \quad (3)$$

228

229 where ρ is the mass density of epoxy modified asphalt mastic, k denotes the thermal
 230 conductivity, c_p is the heat capacity, T is the temperature, Q represents the exothermic heat
 231 source (kW/m^3). It is assumed that the convection and radiation heat do not have important
 232 impact on the energy balance of the system.

233 As the resin turns into a networked microstructure and the epoxy modified bitumen
 234 hardens, heat is released. The heat releasing rate is proportional to the consumption rate of
 235 reactive elements in the epoxy binder. Assuming no heat flow, the volumetric heat source Q
 236 accounts the exothermic hardening effect and is described by :

237

$$Q = \rho \Delta H_{exo} \frac{\partial \alpha}{\partial t} \quad (4)$$

238

239 where ΔH_{exo} is the exothermic reaction heat. The reaction rate gradients generated by the
 240 temperature gradients affect the temperature profile in the hardening material. The
 241 exothermic reaction diagram is shown in **Fig. 1(b)**.

242

243 **Chemo-rheological Equation**

244 The chemical hardening prediction of the epoxy modified bitumen was the ultimate scope of
 245 this study. On molecular level, the viscosity of the epoxy-bitumen is affected by (i) the
 246 increasing temperature, which increases molecular mobility, and (ii) the molecular size
 247 growth and the subsequent crosslinking of molecules. When the average molecular weight
 248 rises towards infinity the viscosity of epoxy-bitumen becomes infinite as well and the gel
 249 point is reached (25). In both network-forming polymerization and the crosslinking of

250 polymeric chains, the gel point is expressed as an extent of chemical reaction. At the gel point
 251 a solid (network) material spanning the entire system is formed. Despite the solidification of
 252 epoxy which occurs at any stage of reaction, gelation of epoxy is a critical event throughout
 253 the crosslinking process that determines the maximum available time before the completion
 254 of pavement construction. Epoxy gelation happens at a distinct extent of hardening reactions,
 255 **Fig. 2.**

256 To predict the chemo-rheological performance of epoxy modified bitumen as function of
 257 time and temperature, the model considers the viscosity changes due to epoxy irreversible
 258 hardening as :

259

$$\eta^*(T, \alpha) = \eta_g^* \cdot \exp \left[-\frac{C_1 (T - T_g(\alpha))}{C_2 + T - T_g(\alpha)} \right] \cdot \left(\frac{\alpha_g}{\alpha_g - \alpha} \right)^{n_r} \quad (5)$$

260

261 where α_g is the extent of reaction at the gel point, $T_g(\alpha)$ is the glass transition temperature of
 262 the uncured material which is a function of the hardening degree, η_g^* is the complex viscosity
 263 at the glass transition temperature, C_1 and C_2 are material-dependent and temperature-
 264 independent constants obtained from the rearranged William-Landel-Ferry (WLF) equation
 265 and n_r is a material-dependent constant. The Eq. (5), which is a combination of the WLF
 266 equation (26) and a conversion term, was obtained by others (27) and describes the chemo-
 267 rheology of an epoxy bituminous blend as function of time and temperature.

268

269 For the determination of the chemo-rheological model, several criteria can be used to
 270 characterize the glass transition temperature in epoxy resins and epoxy modified bitumen in
 271 general. The crossover point between the storage and loss modulus curves the point, where
 272 the loss tangent becomes frequency independent, and the inflection point of the modulus
 273 curve are some of the methods used to determine the glass transition temperature. However,
 274 unlike pure bitumen, epoxy modified binders undergo reactions during hardening leading to
 275 polymerization of the insoluble resinous part of modified bitumen and the slight reduction in
 276 the glass transition temperature. The decrease of glass transition temperature may be caused
 277 by the limited polar interaction of epoxy resin with asphaltene groups of bitumen. Typically,
 278 the glass transition temperature of many epoxy systems is defined using empirical
 279 DiBenedetto equation (28). It should be mentioned that hardening agents are capable of
 280 increasing both the glass transition temperatures of bituminous and resinous phase in the
 epoxy modified bitumen.

281

282 According to previous study (15), the activation energy of epoxy-bitumen was marginally
 283 lower (46-49 kJ/mol) and subsequently released less heat than the pure epoxy (50 kJ/mol)
 284 showing negligible impact of bitumen on chemical hardening reactions, when part of epoxy
 285 was substituted by bitumen. However, in cases where part of the bitumen was substituted
 286 with epoxy, the difference of activation energies of pure epoxy and epoxy modified binders
 287 will be higher, 78 kJ/mol and 65 kJ/mol for epoxy and epoxy modified binders, respectively
 288 (13). The contact opportunities between epoxy and hardening agent are reduced by bitumen
 and the chemical reactions are inhibited leading to higher energy needs.

289

290 **Numerical Simulation of Hardening**

291 For the qualitative analyses, one three-dimensional cubic finite-element mesh of E10-3 m
 292 geometry and of 16200 elements was created. The proposed chemo-rheological model of
 293 epoxy modified bituminous blends suitable for paving applications was implemented in
 294 COMSOL Multiphysics to simulate the viscosity evolution during chemical hardening as a
 295 measure of reaction progress. By varying the different parameters insight is gained into the
 296 effect of each of them on the overall hardening process of epoxy modified binders. For

297 these analyses, the density (1600 kg/m³), heat capacity (920 J/kg·K) and thermal
298 conductivity (0.45 W/m·K) were assumed to be constant (29). The exothermic reaction heat
299 (ΔH_{exo}) was considered constant (100 kJ/kg) as well. Additionally, it is assumed that the glass
300 transition temperature and the gelation of the unreacted epoxy-bituminous binder occurs at a
301 fixed hardening degree (HD) and, since through processing of epoxy modified blend before
302 compaction the material is not fully cured. The viscosity at the glass transition temperature
303 was assumed to be 1 Pa·s. The imposed thermal field at the top boundary of the finite
304 element cube is shown in **Fig. 3** with the rest boundaries to be thermally insulated. The
305 model predictions are demonstrated at a point located in the cubic centre.

306

307 **RESULTS AND DISCUSSION**

308 In order to apply epoxy modified binders for pavement construction successfully, it is
309 necessary to understand the reaction kinetics of epoxy modified bituminous mixes for various
310 processing scenarios from the plant production to transport, laying and compaction of these
311 materials. Continuous monitoring of epoxy reactions in bitumen is highly important to obtain
312 the desired end product performance. The hardening of epoxy-bituminous blends involves
313 heat transfer, cure kinetics phenomena and mechanical changes. This section presents the
314 numerical predictions of HD and viscosity, which very sensitive to molecular changes at the
315 early material hardening stages of epoxy-bituminous binder, blends with various
316 characteristics and under different operational conditions. The findings of the numerical
317 analyses are discussed in the following subsections.

318

319 **Influence of Activation Energy and Reaction Parameters on Hardening Degree**

320 To assess the influence of reaction kinetics on the hardening caused by epoxy polymerization
321 in bituminous binder, the activation energy, the hardening reaction order and the kinetic
322 factor were varied. For the current analyses, values of the kinetic parameters as in previous
323 researches were utilized. From **Fig. 4**, the typical HD evolution at different temperatures is
324 shown. The numerical results after decreasing the activation energy E_a from 80 kJ/mol to 50
325 kJ/mol, subjected to isothermal conditions (100 °C) and with varying the hardening reaction
326 order n (0.2 to 2, step of 0.4) and the kinetic factor k_0 (200 to 1000 1/s, step of 200 1/s) are
327 presented in **Fig. 5**.

328 It is observed that activation energy has a strong impact on HD compared to the other
329 parameters (**Fig. 5**), which can be explained by the influence on the polymerization
330 occurrence and crosslinking of epoxy in the modified binder. As the activation energy
331 decreases, HD increased remarkably. For example, the increase of HD was observed to
332 become 3.94E-01 from 1.72E-02 when the activation energy changes from 60 kJ/mol to 50
333 kJ/mol, for n 0.4 and k_0 600, respectively. This performance is also apparent for higher levels
334 of activation energy and it is related with the type of epoxy components (i.e., hardening agent
335 and epoxy resin) and the chemical interaction between them. A more reactive agent can be
336 attributed to lower the energy demands to trigger the epoxy polymerization. Since bitumen is
337 substituted by epoxy through the modification, increasing the amount of epoxy within the
338 bituminous matrix can increase the contact opportunities of the thermoset phase and results a
339 subsequent increase of crosslinking density. Based on these results, this phenomenon leads to
340 higher epoxy percentages but lower activation energy levels.

341

342 **Influence of Temperature and Reaction Extent on Viscosity Development under**
343 **Isothermal Conditions**

344 The duration at high temperatures of the blend from plant to field will affect the achieved
345 viscosity. To investigate these different isothermal analyses were considered, because of the
346 importance for simulating real practical scenarios. The parameter of chemical reaction extent
347 at the gel point (α_g) was considered to be constant and the numerical analyses were performed
348 with varying this parameter from 0.3 to 0.9 under defining a heat flux related to warm and
349 half-warm mixed production conditions (e.g., 80-120 °C with step of 10 °C) at the boundary.
350 Also, it should be pointed out that normally the reaction kinetics do not change during the
351 occurrence of gelation of epoxy-type blends.

352 The impact of kinetic factor on viscosity development is appeared in the isothermal
353 hardening curves of **Fig. 6(a)** showing that the highly reactive blends harden faster. **Fig. 6(b)**
354 demonstrates the influence of temperature on viscosity achieved after 120 min of hardening.
355 Increase in the predicted viscosity after 120 min hardening was achieved with increasing
356 temperature. The computed results illustrate the role of applied temperatures on material
357 polymerization and on viscosity at isothermal conditions since the material reached a higher
358 HD when the conditioning temperature was higher.

359 The trend above was also observed in previous practical studies (5). The epoxy modified
360 bituminous mixes were produced and compacted at a temperature range substantially lower
361 than for conventional HMA mixes resulting in a decrease of the material production energy
362 and reduction of carbon footprint of the whole pavement manufacturing chain. Therefore,
363 apart from the influence of physical reaction parameters, the rate of polymeric network
364 formation is also a function of temperature which assists in the speed of hardening activation
365 of epoxy in the bituminous matrix. Moreover, a similar trend was observed for α_g , as a
366 material parameter linked with the gel point of epoxy, on building the viscosity of epoxy
367 modified binders (**Fig. 6(b)**). For example, for all the predefined applied temperatures, the
368 achieved viscosity was higher when α_g decreases from 0.9 to 0.3. As a result, if the
369 intermolecular interactions between the epoxy-bitumen components produce a composite
370 with lower value of hardening extent until the material gelation, then the initiation of
371 hardening can be caused with minimum energy demands and the material can be fully cured
372 at a higher rate.

373 In **Fig. 7**, the influence of the constant n_r is depicted showing the importance of this
374 parameter on providing realistic numerical predictions. The rate of viscosity development
375 was found to increase with increasing value of n_r from 2 to 4 with step of 0.5 for the initially
376 un-reacted epoxy modified bitumen having as consequence a faster hardening. Thus, for the
377 ranking of the individual epoxy components and the blend of epoxy with bitumen, it is
378 important to identify experimentally these factors since these contribute vitally on material
379 structural development and on the shape of chemo-rheological plots. The observed trends of
380 predicted viscosity coincide with the similar trends of others (5).

381

382 **Influence of Heating Rate on Viscosity Development under Non-isothermal Conditions**

383 Next, due to the fact that the current model was developed to characterize the performance of
384 material under the usual operating conditions in a hardening cycle (mixing plant to
385 construction field), it is also important to study the evolution of the viscosity at non-
386 isothermal heating mode. Epoxy modified bitumen was analysed from 30 to 80 °C/min with
387 10 °C/min step and the evolution of hardening degree under these applied heating rates is
388 presented in **Fig. 8(a)**. The rising temperature activates reaction between epoxy and
389 hardening agent forming polymeric chains quicker. However, it should be noted that high
390 heating rates can cause undesired temperature differences and irregularities in epoxy
391 chemical hardening. In **Fig. 8(b)**, the predicted viscosity at the first 120 sec of hardening

392 under different heating rates and kinetic factors k_0 , as a very influential reaction parameter
393 regarding previous analyses, is demonstrated. Higher heating rates and k_0 increase the
394 material achieved viscosity. These predicted results can be attributed to the trend of
395 consuming more energy to result quicker material hardening, something which can increase
396 the risk of unwanted issues within the blend as well, such as variation in porosity or epoxy
397 distribution in bituminous phase. Although the material was studied at different heating rates,
398 the viscosity development was non-linear and related with the applied thermal field, which is
399 a common trend identified in all studied cases of these analyses.

400

401 CONCLUSIONS AND FUTURE WORK

402 This paper presents the hardening process and the subsequent predictions of viscosity
403 evolution of epoxy modified bitumen via performing numerical analyses. These analyses
404 showed the impact of all the model parameters on chemical hardening of epoxy blends.
405 Particularly, results of the analyses suggest that lower levels of activation energy increase the
406 degree of hardening and the rate of viscosity development. In addition, the performed
407 numerical sensitivity analyses have shown that with the increase of temperature the material
408 viscosity increased, whereas the polymerization rate was highly dependent on the
409 temperature. By decreasing the hardening reaction until the gel point the achieved viscosity
410 of epoxy modified bitumen, after a certain isothermal hardening period, was increased which
411 shows the importance of gel reaction extent on material viscosity evolution.

412 In the near future, the proposed model will be verified through differential scanning
413 calorimetry (DSC) tests at (non-) isothermal conditions. All the reactions should be evaluated
414 to quantify the temperature dependence of kinetic parameters under different heating modes.
415 The glass transition of epoxy modified bituminous binders and their behaviour need to be
416 measured to plan sufficiently the field operations mainly because the manufacturing and the
417 delivering conditions of the mixes have direct impact on long-term pavement performance.
418 Once the DSC studies will be developed, they can be used to optimize performance-related
419 details of epoxy modified bituminous pavements design.

420

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492

493 **LIST OF FIGURES**

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510

511 **FIGURE 6** Predicted viscosity development of epoxy modified bitumen for : (a)
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514

515 **FIGURE 7** Predicted viscosity development of epoxy modified bitumen under
516 isothermal heating conditions for different n_r at $T=100$ °C ($E_a=50$ kJ/mol, $n=0.2$, $k_0=100$
517 1/s, $\alpha_g=0.6$)

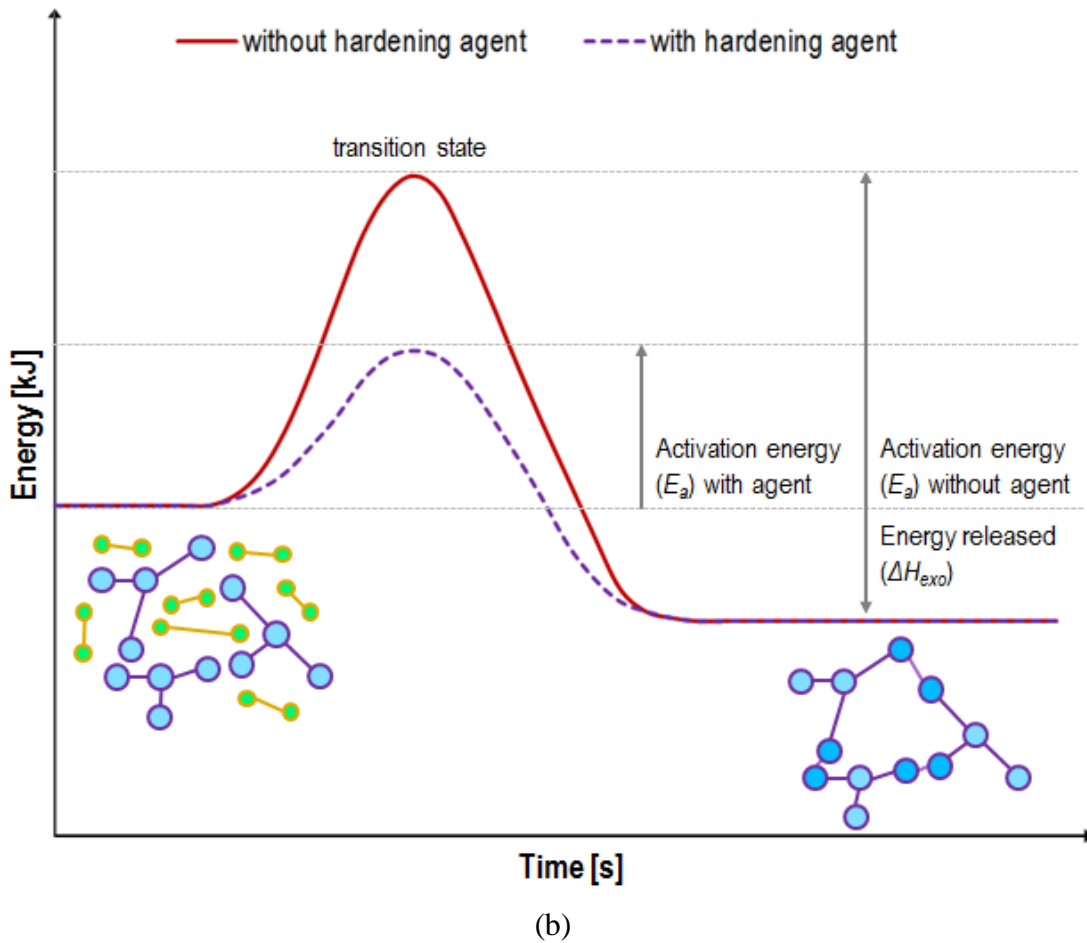
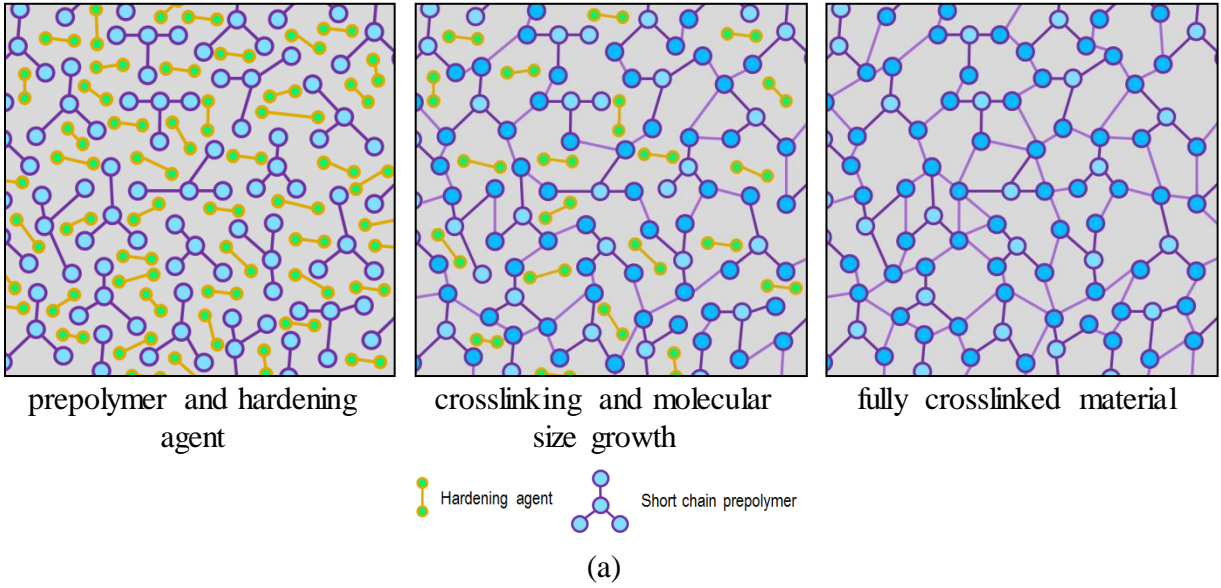
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519 **FIGURE 8** Non-isothermal chemical hardening of epoxy modified bitumen: (a)
520 predicted hardening degree development of epoxy modified bitumen ($E_a=50$ kJ/mol,
521 $n=0.2$, $k_0=200$ 1/s, $\alpha_g=0.6$) and (b) predicted viscosity with various heating rates and
522 kinetic factor k_0 after 2 min hardening

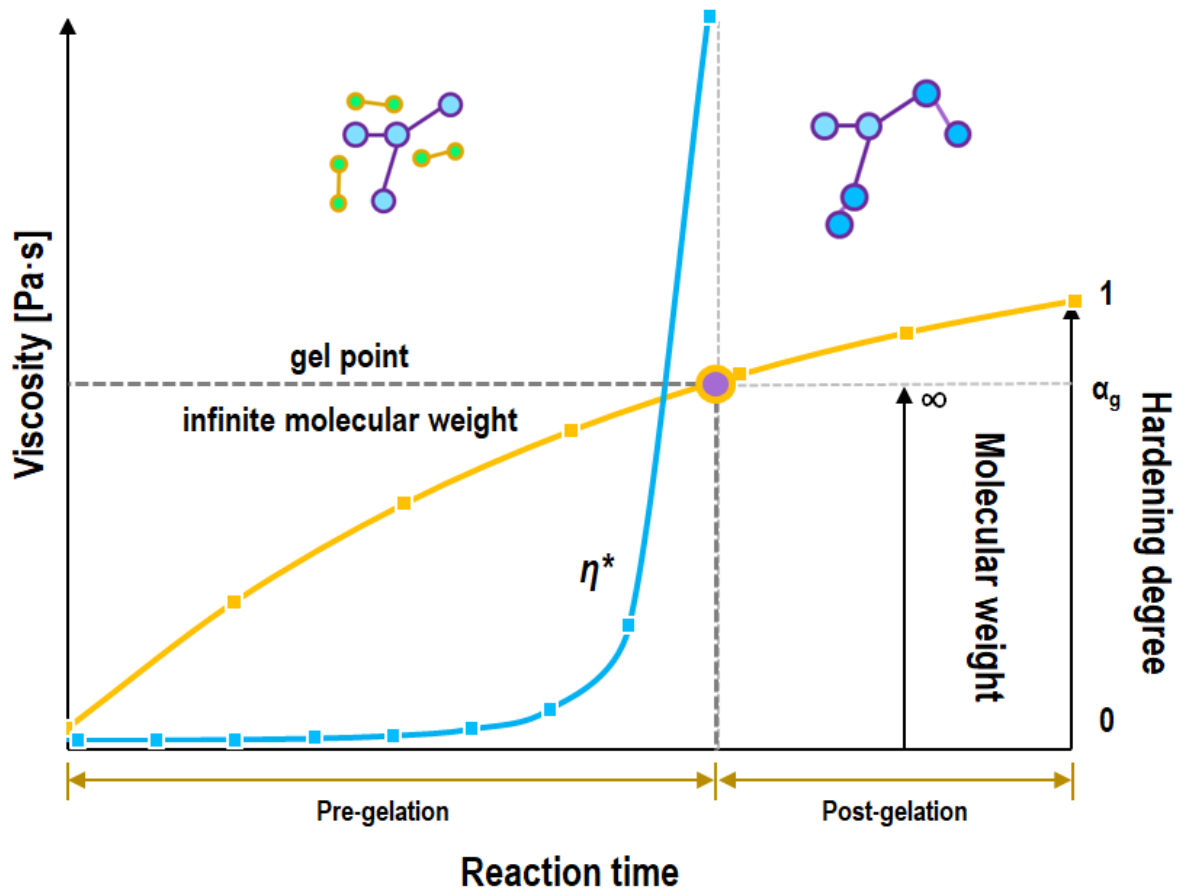
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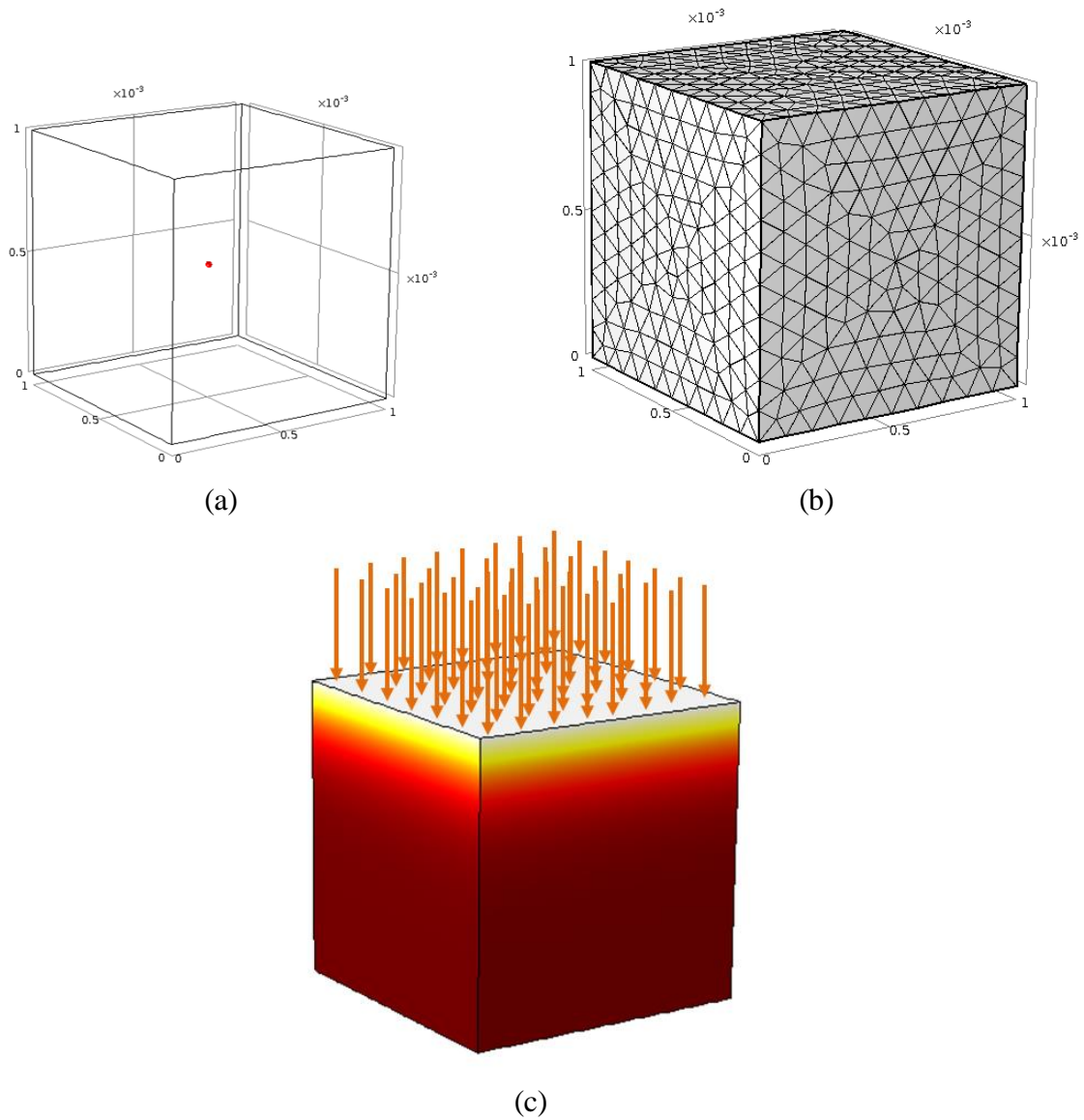


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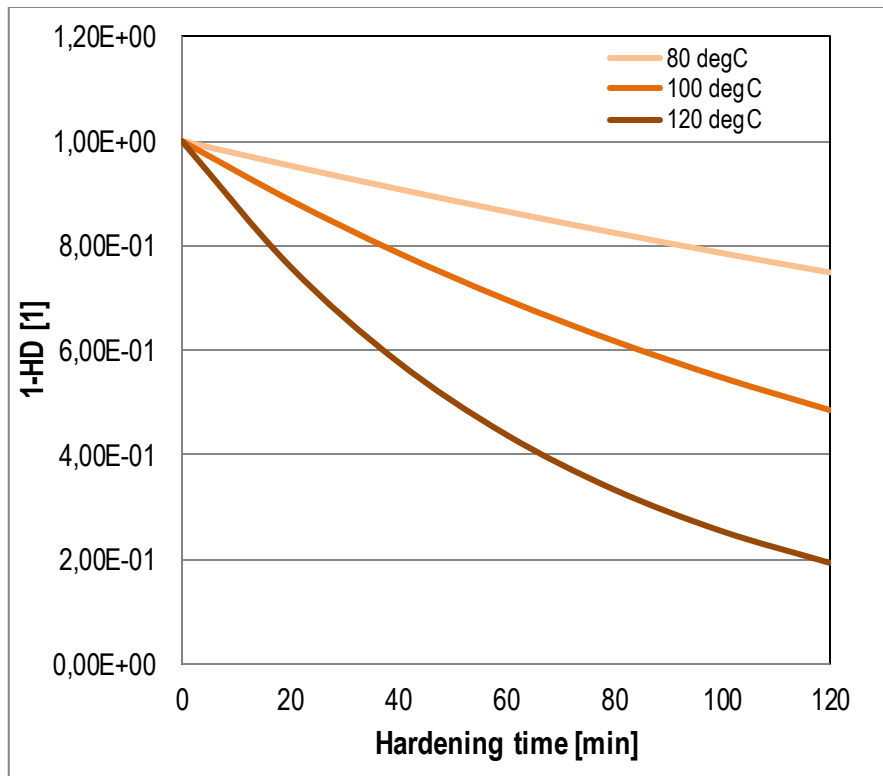


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FIGURE 2 Schematic of variation of epoxy modified bitumen properties during isothermal chemical hardening

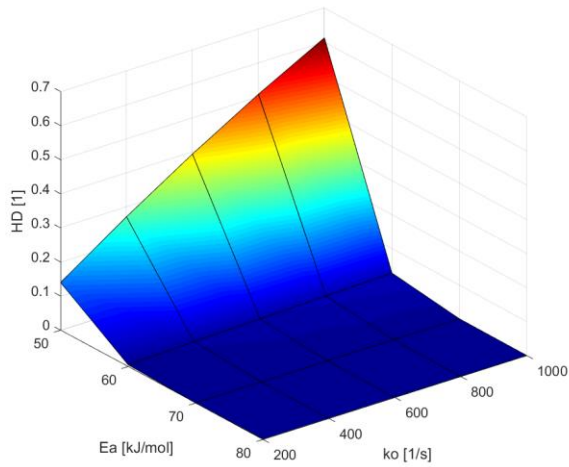


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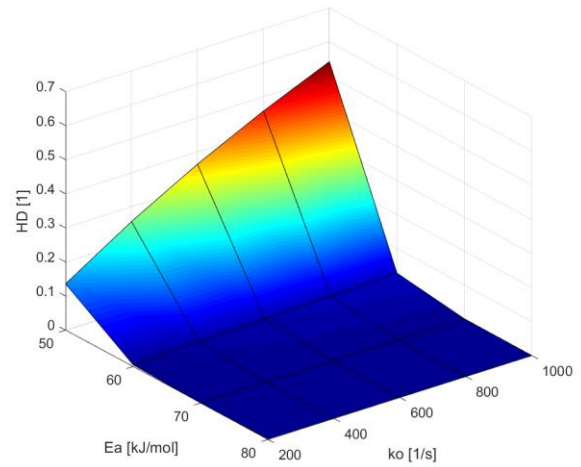


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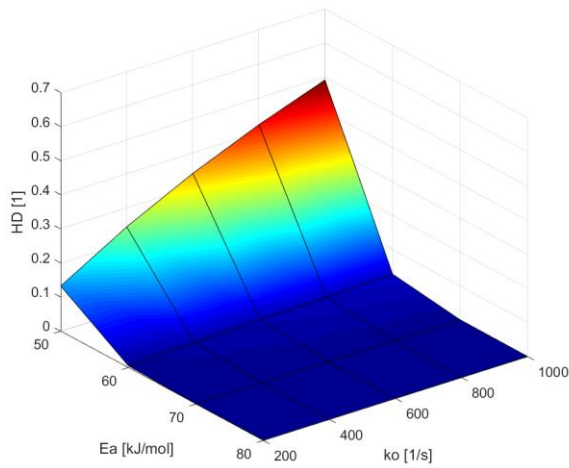
FIGURE 4 Typical isothermal hardening of epoxy modified bitumen for different heating temperatures ($E_a=50$ kJ/mol, $n=1$, $k_0=100$ 1/s)



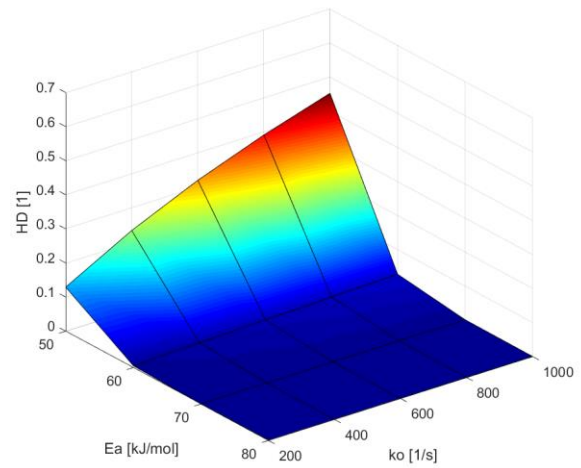
(a)



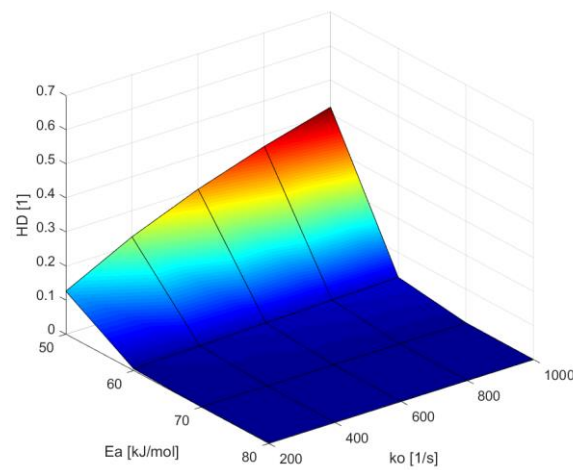
(b)



(c)

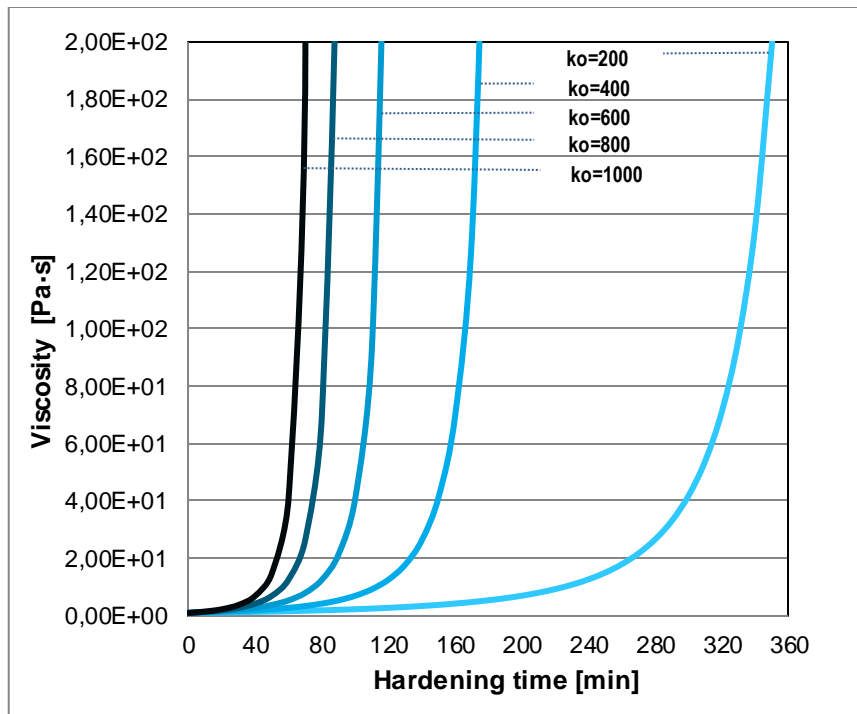


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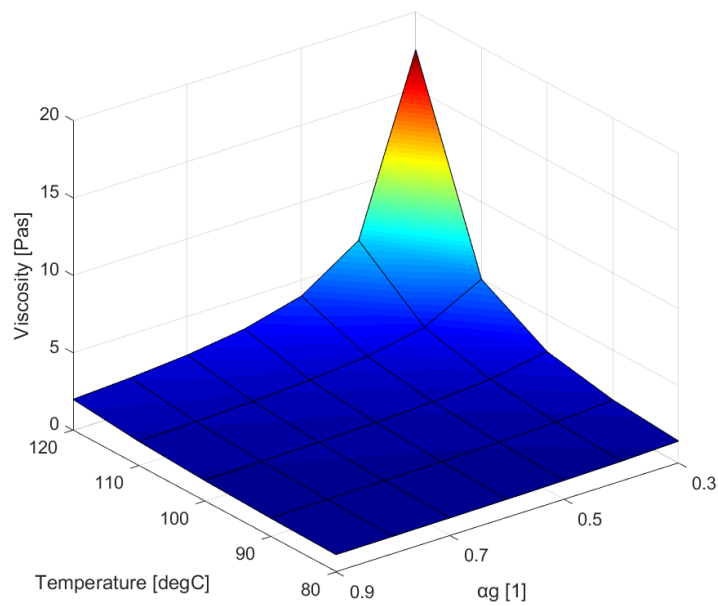


(e)

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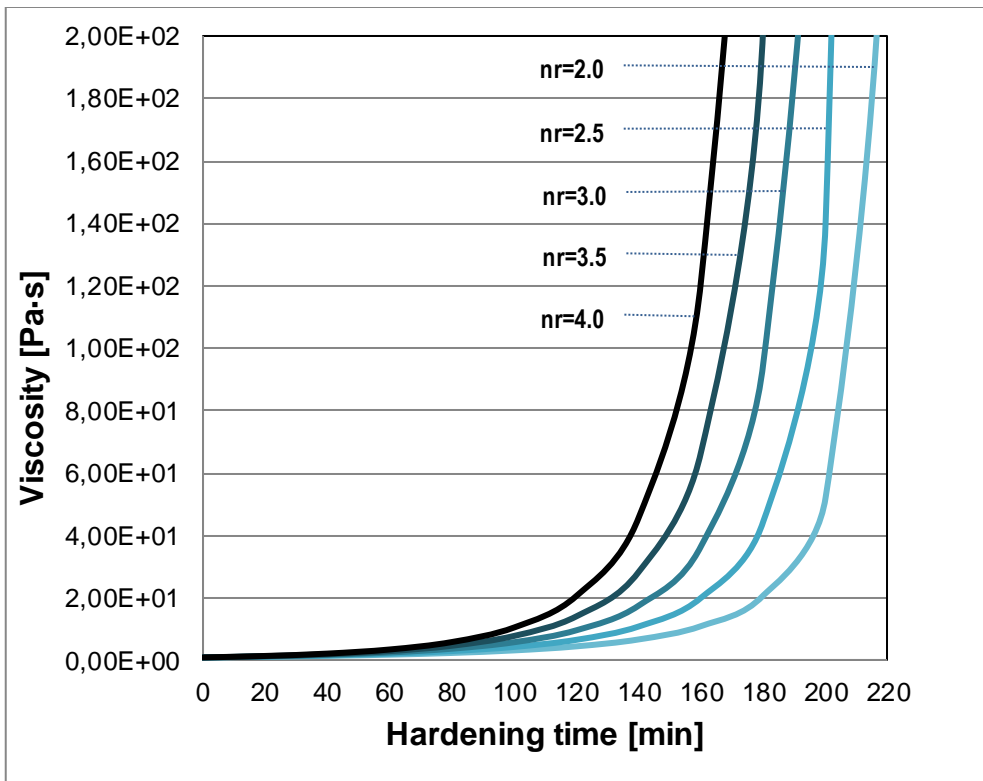


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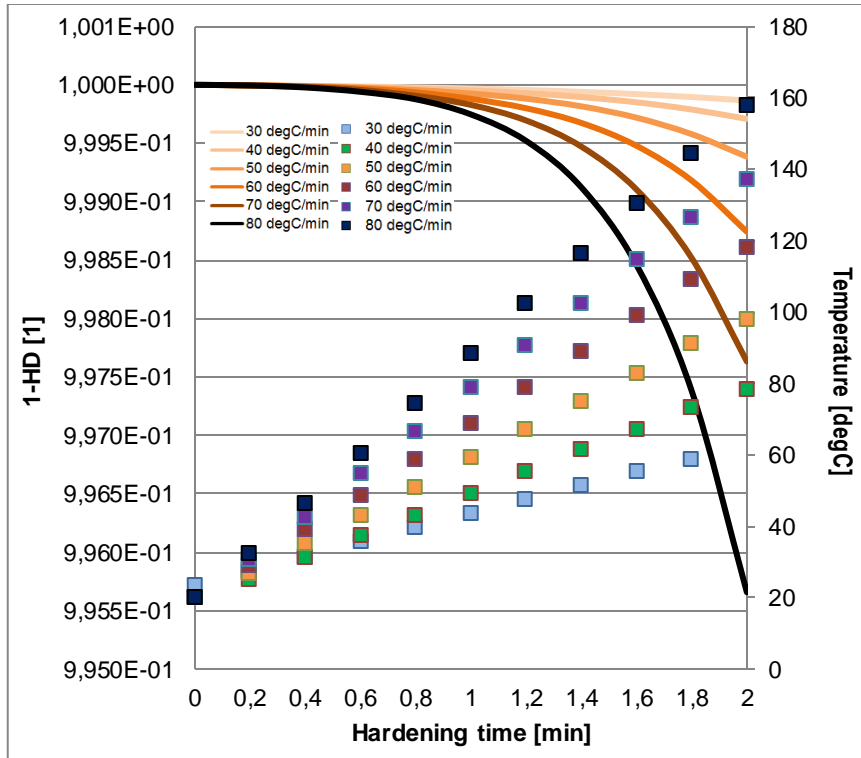
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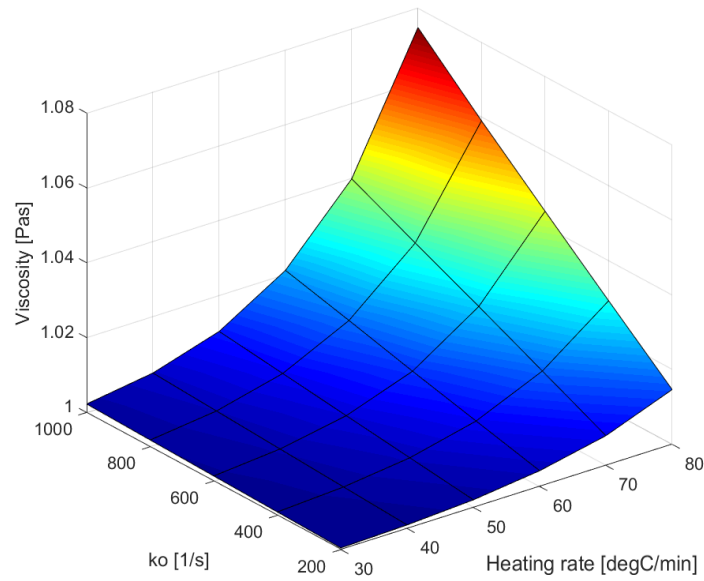


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FIGURE 7 Predicted viscosity development of epoxy modified bitumen under isothermal heating conditions for different n_r at $T=100\text{ }^\circ\text{C}$ ($E_a=50\text{ kJ/mol}$, $n=0.2$, $k_0=100\text{ 1/s}$, $\alpha_g=0.6$)



(a)



(b)

559 **FIGURE 8** Non-isothermal chemical hardening of epoxy modified bitumen: (a)
 560 predicted hardening degree development of epoxy modified bitumen ($E_a=50$ kJ/mol,
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