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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 remelted 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  $\alpha$  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  $\rho$  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 ( $\text{kW}/\text{m}^3$ ). 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  $\Delta H_{exo}$  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 :

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

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

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

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

## 289 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/m<sup>3</sup>), 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 ( $\Delta H_{exo}$ ) 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 ( $\alpha_g$ ) 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  $\alpha_g$ , 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  $\alpha_g$  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

## 421 **REFERENCES**

- 422 1. Widyatmoko, I., B. Zhao, R.C. Elliott, W.G. Lloyd. Curing Characteristics and the  
423 Performance of Epoxy Asphalts. *Presented at Tenth International Conference on*  
424 *Asphalt Pavements*, Quebec, Canada, 2006.
- 425 2. Herrington, P., D. Alabaster. Epoxy Modified Open-graded Porous Asphalt. *Road*  
426 *Materials and Pavement Design* 9(3), 2008, pp. 481-498.
- 427 3. Xiao, Y., M.F.C. van de Ven, A.A.A. Molenaar, Z. Su, F. Zandvoort. Characteristics of  
428 Two-component Epoxy Modified Bitumen. *Materials and Structures* 44(3), 2010, pp.  
429 611-622.
- 430 4. Wei, J., Y. Zhang. Study on the Curing Process of Epoxy Asphalt. *Journal of Testing*  
431 *and Evaluation* 40(7), 2012, pp. 1-8.
- 432 5. Yin, C., H. Zhang, Y. Pan. Cracking Mechanism and Repair Techniques of Epoxy  
433 Asphalt on Steel Bridge Deck Pavement. *Transportation Research Record*, No. 2550,  
434 National Research Council, Washington, D.C., 2016, pp. 123-130.
- 435 6. International Transport Forum. *Long-life Surfacing for Roads: Field Test Results*. ITF  
436 Research Reports, OECD, Paris, France, 2017.
- 437 7. Redelius, P.G. Solubility Parameters and Bitumen. *Fuel* 79, 2000, pp. 27-35.
- 438 8. Harper, C.A., *Handbook of Plastics, Elastomers and Composites*. McGraw-Hill, New  
439 York, 1996.
- 440 9. Odian, G. *Principles of Polymerization*. John Wiley & Sons: New York, 1981.

- 441 10. Yu, J.Y., P.L. Cong, S.P. Wu. Laboratory Investigation of the Properties of Asphalt  
442 Modified with Epoxy Resin. *Journal of Applied Polymer Science* 113, 2009, pp. 3557-  
443 3563.
- 444 11. Luo, S., Q. Lu, Z. Qian. Performance Evaluation of Epoxy Modified Open-graded  
445 Porous Asphalt Concrete. *Construction and Building Materials* 76, 2015, pp. 97-102.
- 446 12. Zhou, W., H. Zhao, J. Wen, F.C. Cai, N. Ma, T. Jiang. Study on Effects of Flexible  
447 Curing Agent on the Structure and Performance of Epoxy-asphalt. *Journal of Wuhan*  
448 *University of Technology* 33(7), 2011, pp. 28-31.
13. Li, S., K. Huang, X. Yang, M. Li, J. Xia. Design, Preparation and Characterization of  
Novel Toughened Epoxy Asphalt Based on a Vegetable Oil Derivative for Bridge Deck  
Paving. *Royal Society of Chemistry* 4, 2014, pp. 44741-49.
- 449 14. Kang, Y., F. Wang, Z.M. Chen. Reaction of Asphalt and Maleic Anhydride: Kinetics  
450 and Mechanism. *Chemical Engineering Journal* 164, 2010, pp. 230-237.
- 451 15. Yin, H. H. Jin, C. Wang, Y. Sun, Z. Yuan, H. Xie, Z. Wang, R. Cheng. Thermal,  
452 Damping, and Mechanical Properties of Thermosetting Epoxy-modified Asphalts.  
453 *Journal of Thermal Analysis and Calorimetry* 115, 2014, pp. 1073–1080.
- 454 16. Kang, Y., Q. Wu, R. Jin, P. Yu, J. Cheng. Rubber-like Quasi-thermosetting  
455 Polyetheramine-cured Epoxy Asphalt Composites Capable of Being Opened to Traffic  
456 Immediately. *Scientific Report* 6, 2016, 18882.
- 457 17. Anderson, D. A., D. W. Christensen, H. U. Bahia, R. Dongre, M. G. Sharma, C. E.  
458 Antle, J. Button. *SHRP-A-369: Binder Characterization and Evaluation, Vol. 3:*  
459 *Physical Characterization*. TRB, National Research Council, Washington, D.C., 1994.
- 460 18. Anderson, D. A., M. O. Marasteanu. Physical Hardening of Asphalt Binders Relative to  
461 Their Glass Transition Temperatures. *Transportation Research Record, No. 1661*,  
462 National Research Council, Washington, D.C., 1999, pp. 27–34.
- 463 19. Kamal, M.R., S. Sourour. Kinetics and Thermal Characterization of Thermoset Cure.  
464 *Polymer Engineering and Science* 13(1), 1973, pp. 59-64.
- 465 20. Ryan, M.E., A. Dutta. Kinetics of Epoxy Cure: A Rapid Technique for Kinetic  
466 Parameter Estimation. *Polymer* 20, 1978, pp. 203-206.
- 467 21. Halley, P.J., M.E. Mackay. Chemorheology of Thermosets-An Overview. *Polymer*  
468 *Engineering and Science* 36(5), 1996, pp. 593-609.
- 469 22. Yousefi, A., P.G. Lafleur. Kinetic Studies of Thermoset Cure Reactions: A Review.  
470 *Polymer Composites* 18(2), 1997, pp. 157-168.
- 471 23. Yang, Y., H. Fujiwara, T. Chiba, T. Inoue. Morphology Development in a  
472 Thermoset/Thermoplastic Blend: DAP/PPE System via Apparent Two-step Spinodal  
473 Decomposition. *Polymer* 39(13), 1998, pp. 2745-50.
- 474 24. Blanco, I., G. Cicala, O. Motta, A. Recca. Influence of a Selected Hardener on the  
475 Phase Separation in Epoxy/Thermoplastic Polymer Blends. *Journal of Applied Polymer*  
476 *Science* 94, 2004, pp. 361-371.
- 477 25. Flory, P.J. Molecular Size Distribution in Three Dimensional Polymers. II.  
478 Trifunctional Branching Units. *Journal of the American Chemical Society* 63(11), 1941,  
479 pp. 3091-3096.
- 480 26. Williams, M.L., R.F. Landel, J.D. Ferry. The Temperature Dependence of Relaxation  
481 Mechanisms in Amorphous Polymers and Other Glass-forming Liquids. *Journal of the*  
482 *American Chemical Society* 77(14), 1955, pp. 3701-3707.
- 483 27. Castro, J.M., C.W. Macosko. Kinetics and Rheology of Typical Polyurethane Reaction  
484 Injection Molding Systems. *Society of Polymer Engineers Technical Paper* 26, pp. 434-  
485 438.

- 486 28. DiBenedetto, A.T. Prediction of the Glass Transition Temperature of Polymers: A  
487 Model Based on the Principle of Corresponding States. *Journal of Polymer Science,*  
488 *Part B: Polymer Physics* 25(9), 1987, pp. 1949-1969.
- 489 29. Apostolidis, P., X. Liu, A. Scarpas, C. Kasbergen, M.F.C. van de Ven. Advanced  
490 Evaluation of Asphalt Mortar for Induction Healing Purposes. *Construction and*  
491 *Building Materials* 126, 2016, pp. 9-25.  
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493 **LIST OF FIGURES**

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500

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510

511 **FIGURE 6** Predicted viscosity development of epoxy modified bitumen for : (a)  
512 different  $k_0$  and (b) different  $\alpha_g$  at various temperatures ( $E_a=50$  kJ/mol,  $n=0.2$ ,  $k_0=100$   
513 1/s)

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,  $\alpha_g=0.6$ )

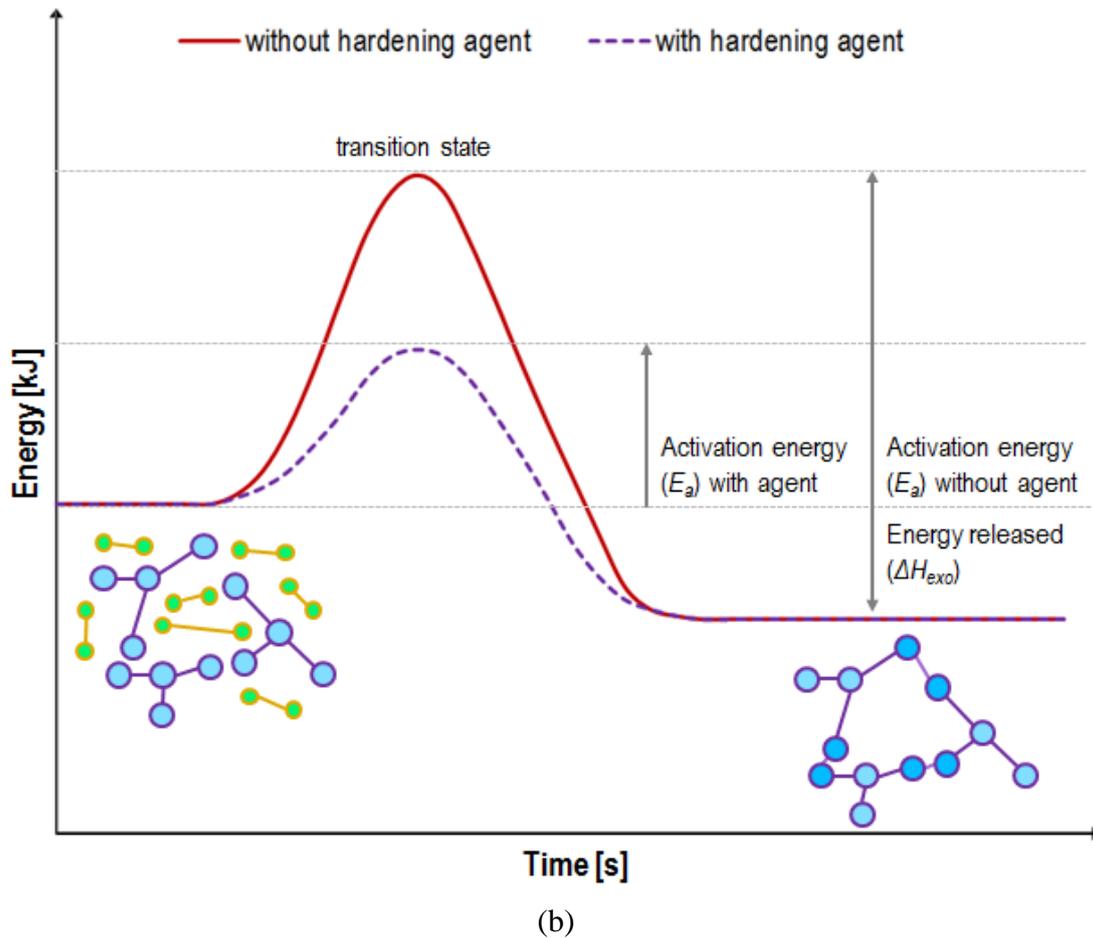
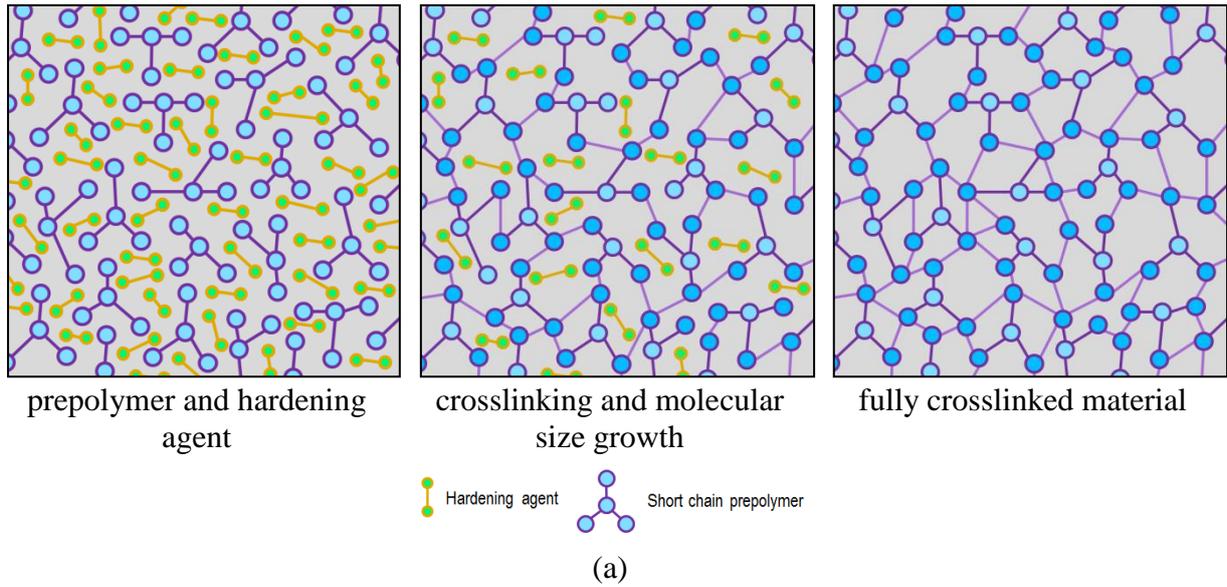
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519 **FIGURE 8** Non-isothermal chemical hardening of epoxy modified bitumen: (a)  
520 predicted hardening degree development of epoxy modified bitumen ( $E_a=50$  kJ/mol,  
521  $n=0.2$ ,  $k_0=200$  1/s,  $\alpha_g=0.6$ ) and (b) predicted viscosity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

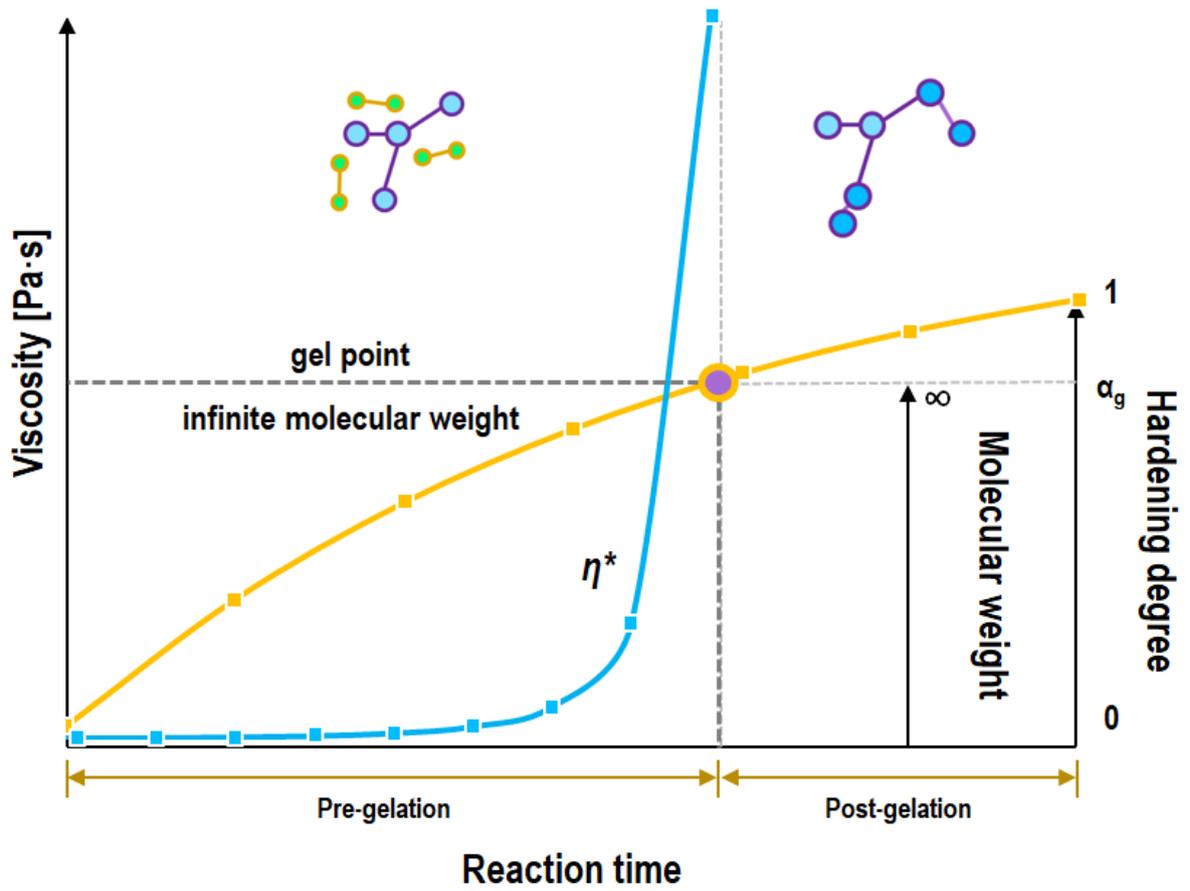
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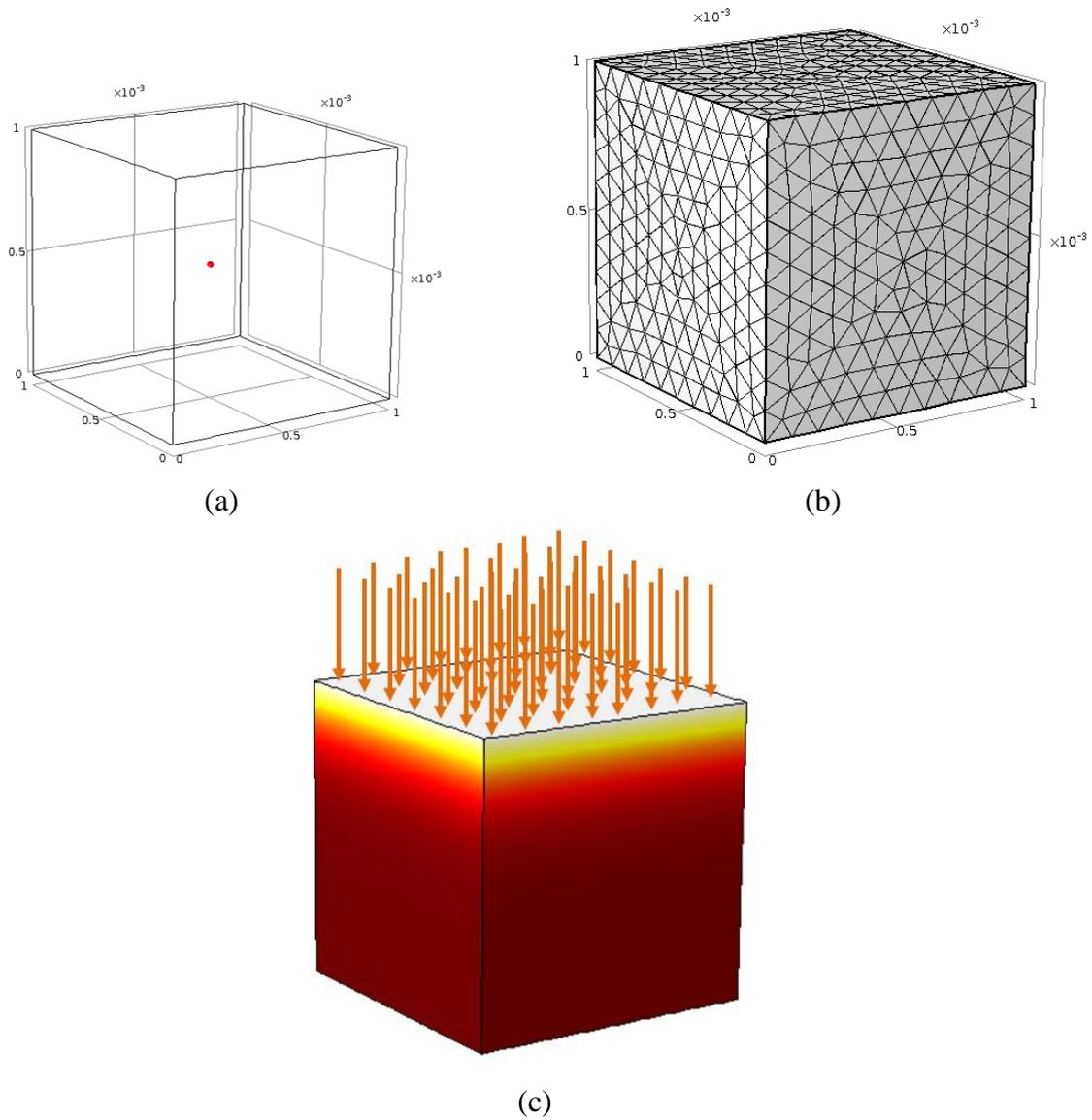


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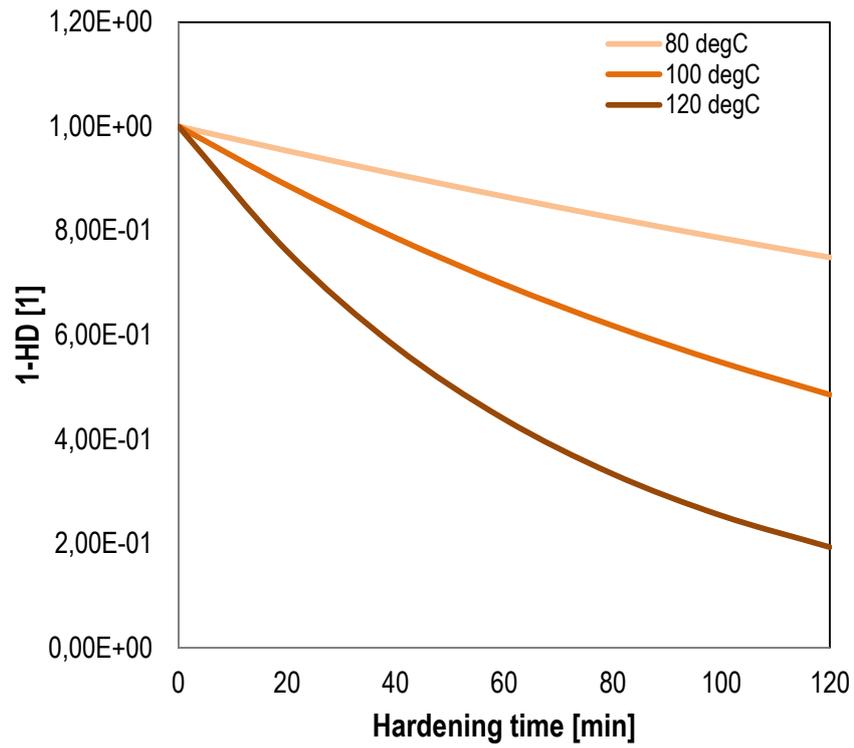


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**FIGURE 2** Schematic of variation of epoxy modified bitumen properties during isothermal chemical hardening

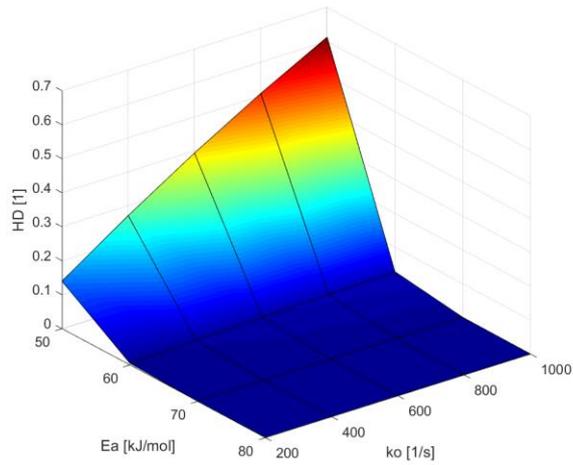


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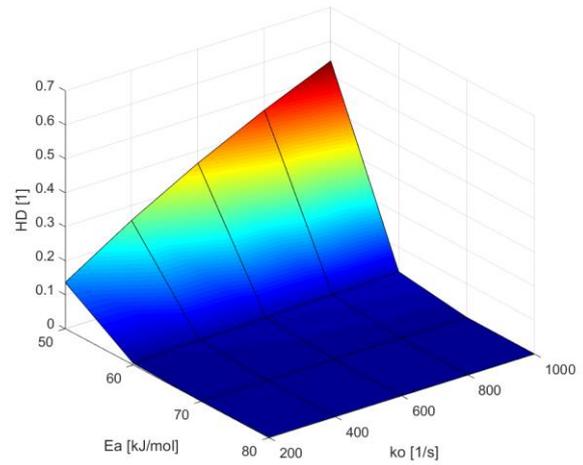


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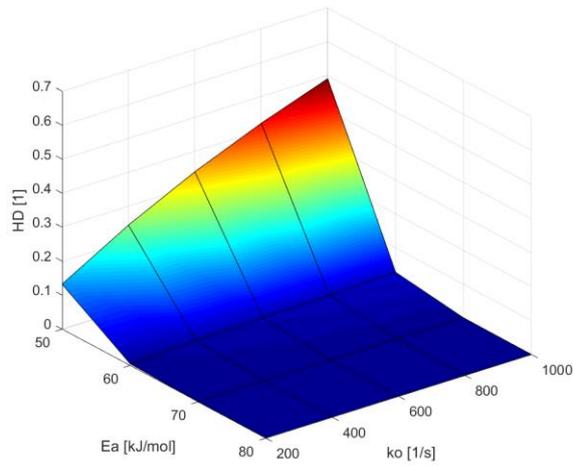
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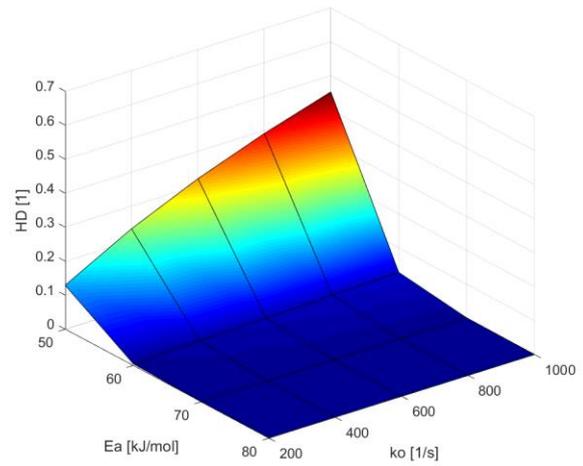
(a)



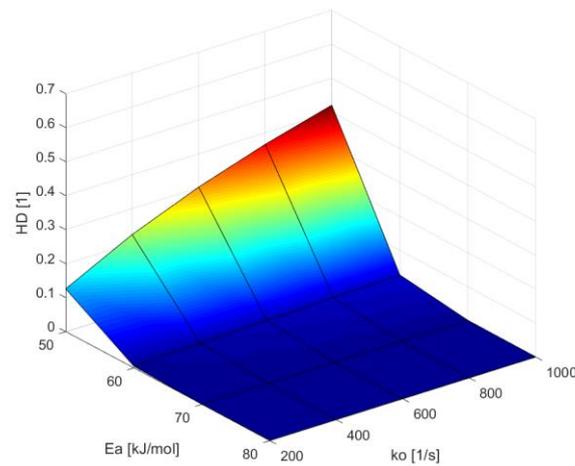
(b)



(c)



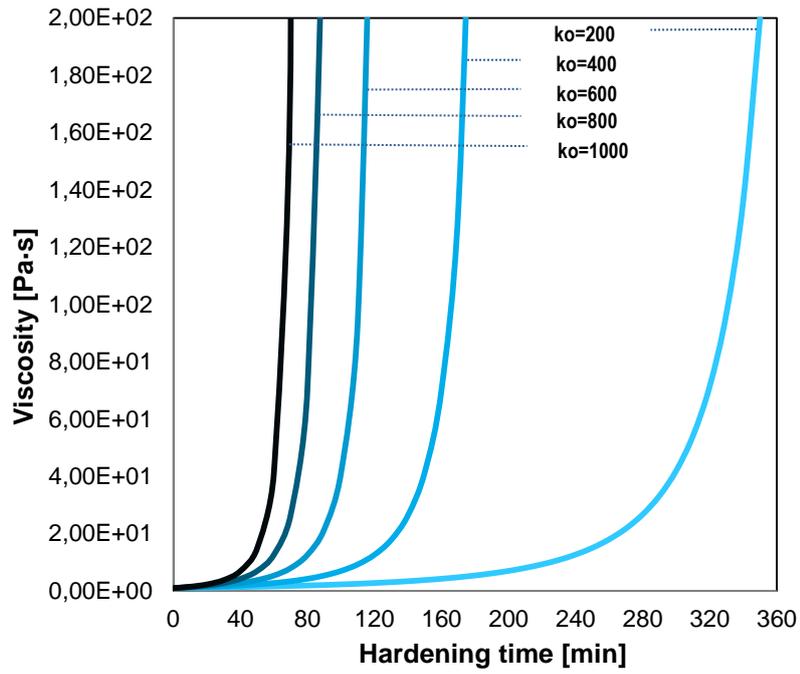
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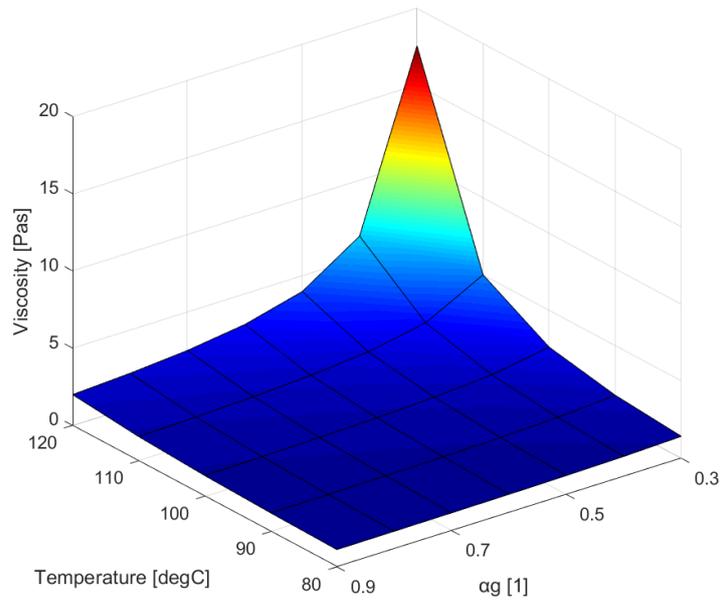
(e)

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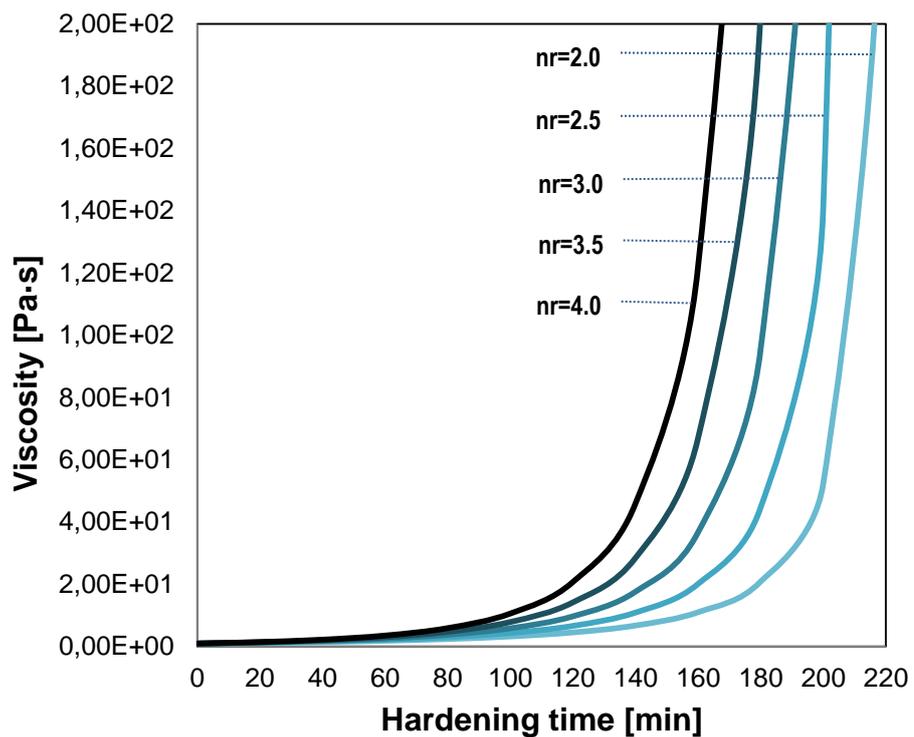


(a)



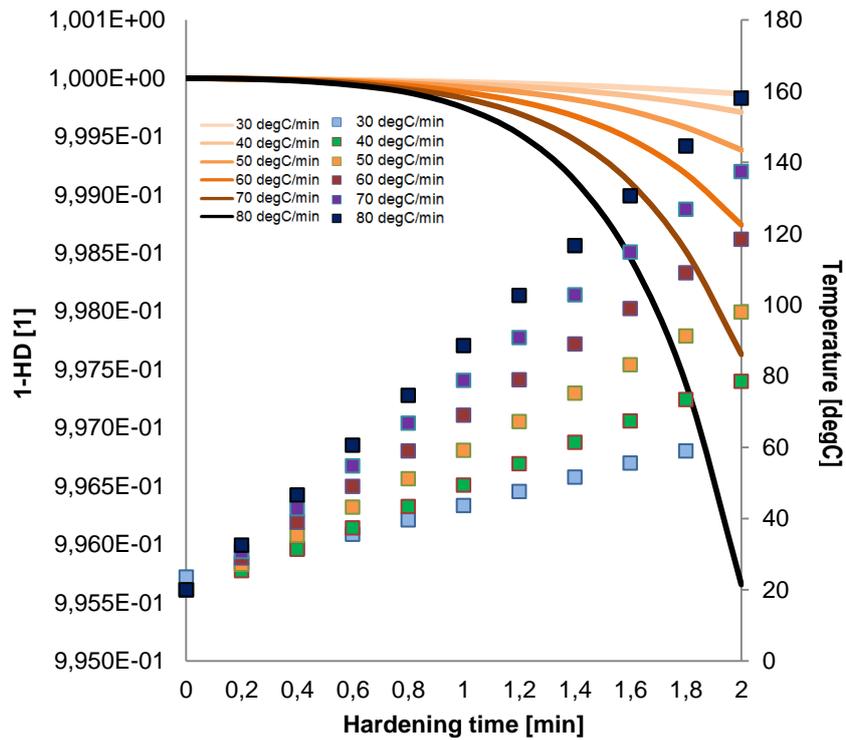
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 551 **1/s)**  
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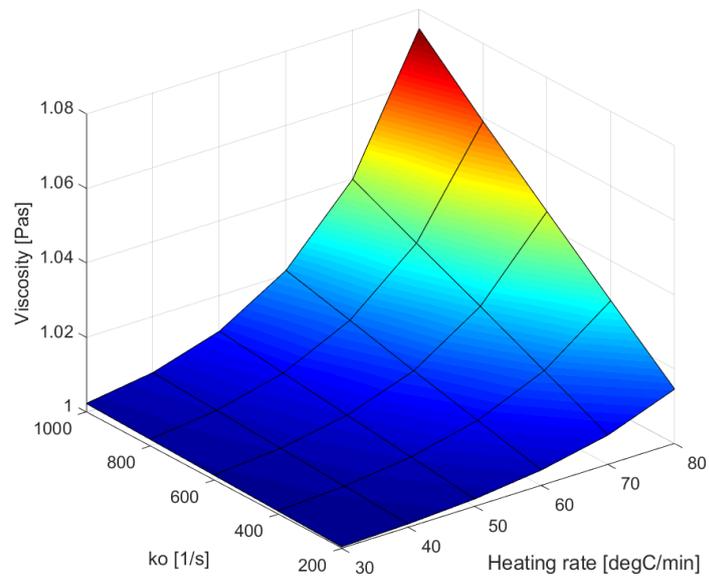


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**FIGURE 7** Predicted viscosity development of epoxy modified bitumen under isothermal heating conditions for different  $n_r$  at  $T=100\text{ }^\circ\text{C}$  ( $E_a=50\text{ kJ/mol}$ ,  $n=0.2$ ,  $k_0=100\text{ 1/s}$ ,  $\alpha_g=0.6$ )



(a)



(b)

559 **FIGURE 8 Non-isothermal chemical hardening of epoxy modified bitumen: (a)**  
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 562 **kinetic factor  $k_0$  after 2 min hardening**