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

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ABSTRACT

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

INTRODUCTION

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

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

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

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

EPOXY MODIFIED BITUMINOUS BINDERS

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

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 ^{o}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 ^{o}C. It is reported in the literature that methyl tetrahydropthalic of cyclic molecular structure, methyl hexahydropthalic and tung oil anhydrides improve the compatilibity 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 tetrahydropthalic 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 ^{o}C or 3d at 60 ^{o}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 ^{o}C or 3d at 60 ^{o}C) for paving applications (*16*). It is believed that the performance of this hardener is related to the light crosslinked networks formed within the bituminous matrix.

MOTIVATION AND OBJECTIVES

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

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

MODELING OF EPOXY MODIFIED BITUMEN HARDENING

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

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

Governing Hardening Kinetics Equation

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

$$\frac{\partial a}{\partial t} = K(T) \cdot f(a) \tag{1}$$

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

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

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

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

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

Governing Heat Transfer Equations

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

$$\rho c_p \nabla T - \nabla \cdot (k \nabla T) = Q \tag{3}$$

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

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

$$Q = \rho \Delta H_{exo} \frac{\partial a}{\partial t} \tag{4}$$

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

Chemo-rheological Equation

The chemical hardening prediction of the epoxy modified bitumen was the ultimate scope of this study. On molecular level, the viscosity of the epoxy-bitumen is affected by (i) the increasing temperature, which increases molecular mobility, and (ii) the molecular size growth and the subsequent crosslinking of molecules. When the average molecular weight rises towards infinity the viscosity of epoxy-bitumen becomes infinite as well and the gel point is reached (*25*). In both network-forming polymerization and the crosslinking of polymeric chains, the gel point is expressed as an extent of chemical reaction. At the gel point a solid (network) material spanning the entire system is formed. Despite the solidification of epoxy which occurs at any stage of reaction, gelation of epoxy is a critical event throughout the crosslinking process that determines the maximum available time before the completion of pavement construction. Epoxy gelation happens at a distinct extent of hardening reactions, **Fig. 2**.

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

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

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

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

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

Numerical Simulation of Hardening

For the qualitative analyses, one three-dimensional cubic finite-element mesh of E10-3 m geometry and of 16200 elements was created. The proposed chemo-rheological model of epoxy modified bituminous blends suitable for paving applications was implemented in COMSOL Multiphysics to simulate the viscosity evolution during chemical hardening as a measure of reaction progress. By varying the different parameters insight is gained into the effect of each of them on the overall hardening process of epoxy modified binders. For these analyses, the density (1600 kg/m3), heat capacity (920 J/kg·K) and thermal conductivity (0.45 W/m·K) were assumed to be constant (*29*). The exothermic reaction heat (ΔH_{exo}) was considered constant (100 kJ/kg) as well. Additionally, it is assumed that the glass transition temperature and the gelation of the unreacted epoxy-bituminous binder occurs at a fixed hardening degree (HD) and, since through processing of epoxy modified blend before compaction the material is not fully cured. The viscosity at the glass transition temperature was assumed to be 1 Pa·s. The imposed thermal field at the top boundary of the finite element cube is shown in **Fig. 3** with the rest boundaries to be thermally insulated. The model predictions are demonstrated at a point located in the cubic centre.

RESULTS AND DISCUSSION

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

Influence of Activation Energy and Reaction Parameters on Hardening Degree

To assess the influence of reaction kinetics on the hardening caused by epoxy polymerization in bituminous binder, the activation energy, the hardening reaction order and the kinetic factor were varied. For the current analyses, values of the kinetic parameters as in previous researches were utilized. From **Fig. 4**, the typical HD evolution at different temperatures is shown. The numerical results after decreasing the activation energy E_a from 80 kJ/mol to 50 kJ/mol, subjected to isothermal conditions (100 °C) and with varying the hardening reaction 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 presented in **Fig. 5**.

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

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

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

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

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

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

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

Next, due to the fact that the current model was developed to characterize the performance of material under the usual operating conditions in a hardening cycle (mixing plant to construction field), it is also important to study the evolution of the viscosity at non-isothermal heating mode. Epoxy modified bitumen was analysed from 30 to 80 ^{o}C/min with 10 ^{o}C/min step and the evolution of hardening degree under these applied heating rates is presented in **Fig. 8(a)**. The rising temperature activates reaction between epoxy and hardening agent forming polymeric chains quicker. However, it should be noted that high heating rates can cause undesired temperature differences and irregularities in epoxy chemical hardening. In **Fig. 8(b),** the predicted viscosity at the first 120 sec of hardening under different heating rates and kinetic factors k_0, as a very influential reaction parameter regarding previous analyses, is demonstrated. Higher heating rates and k_0 increase the material achieved viscosity. These predicted results can be attributed to the trend of consuming more energy to result quicker material hardening, something which can increase the risk of unwanted issues within the blend as well, such as variation in porosity or epoxy distribution in bituminous phase. Although the material was studied at different heating rates, the viscosity development was non-linear and related with the applied thermal field, which is a common trend identified in all studied cases of these analyses.

CONCLUSIONS AND FUTURE WORK

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

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

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LIST OF FIGURES

FIGURE 1 Crosslinking of epoxy modified bitumen: (a) stepwise polymerization of epoxy in the bituminous matrix; and (b) exothermic chemical reaction diagram

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

FIGURE 3 Finite element cubic geometry: (a) location of output point in the centre of cube; (b) mesh and (c) direction of applied thermal field at the top boundary

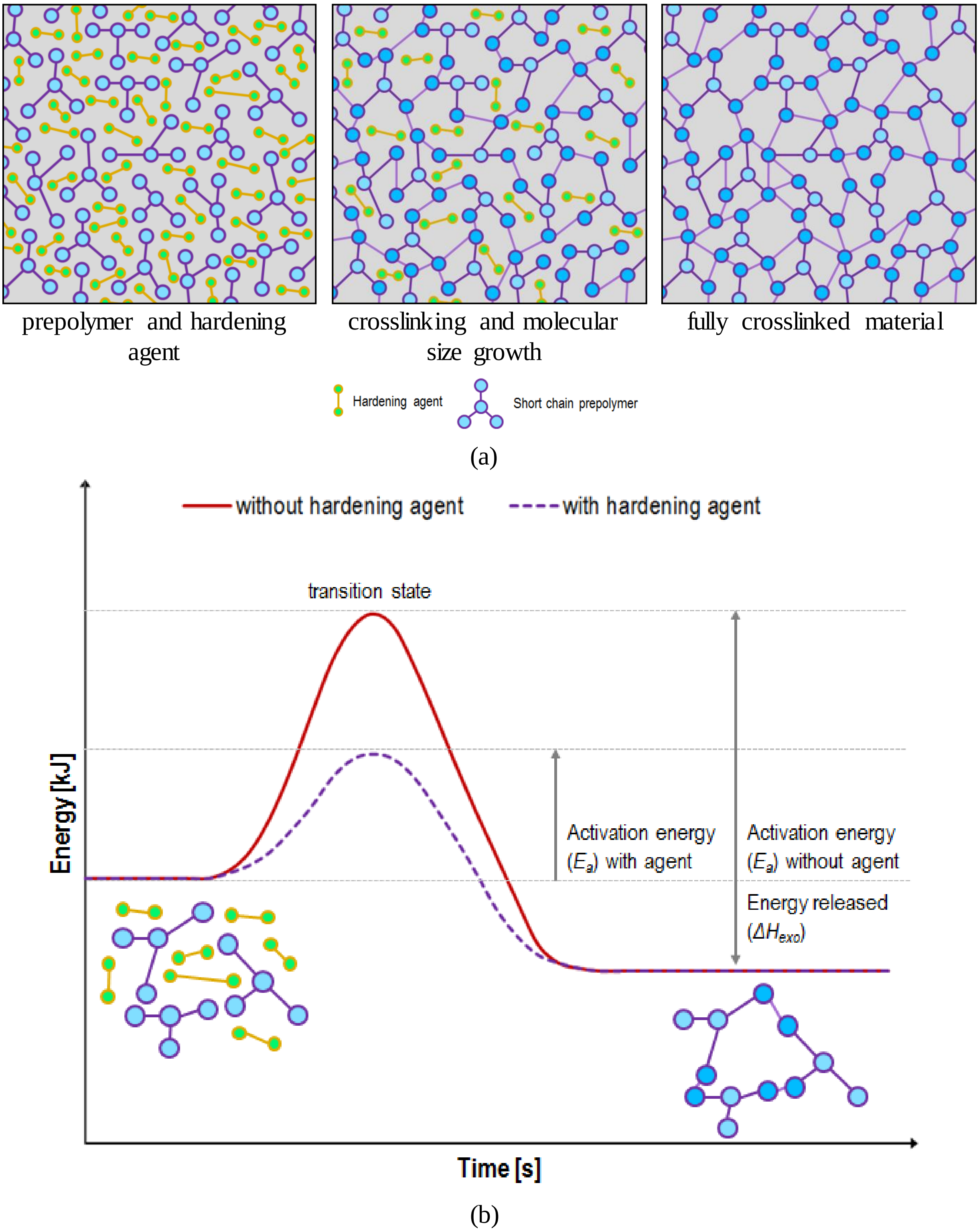
FIGURE 4 Typical isothermal hardening of epoxy modified bitumen for different heating temperatures (E_a=50 kJ/mol, n=1, k_0=100 1/s)

FIGURE 5 Variation of hardening degree for different activation energies and kinetic factors with reaction orders of (a) 0.4, (b) 0.8, (c) 1.2, (d) 1.6 and (e) 2.0 (T=100 ^{o}C and 120 min)

FIGURE 6 Predicted viscosity development of epoxy modified bitumen for : (a) different k_0 and (b) different α_g at various temperatures (Ea=50 kJ/mol, n=0.2, k_0=100 1/s)

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

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



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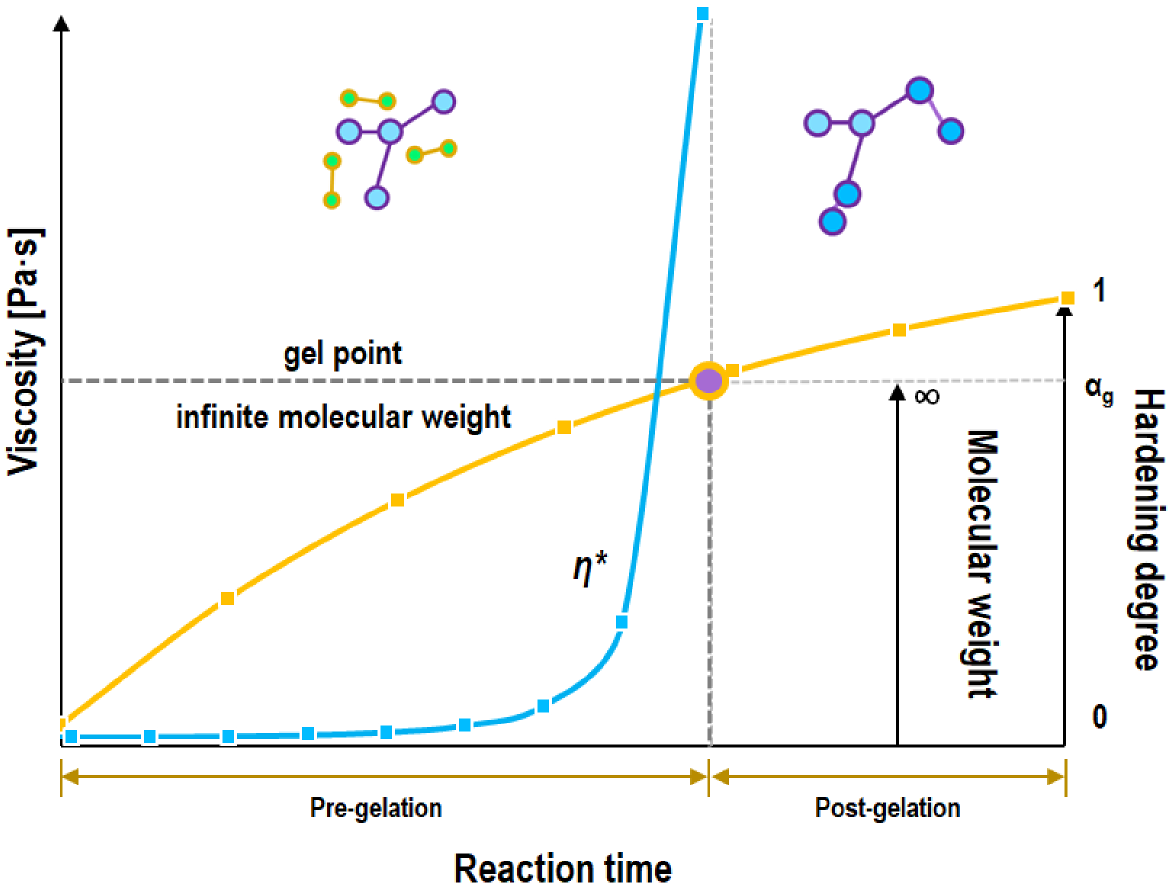
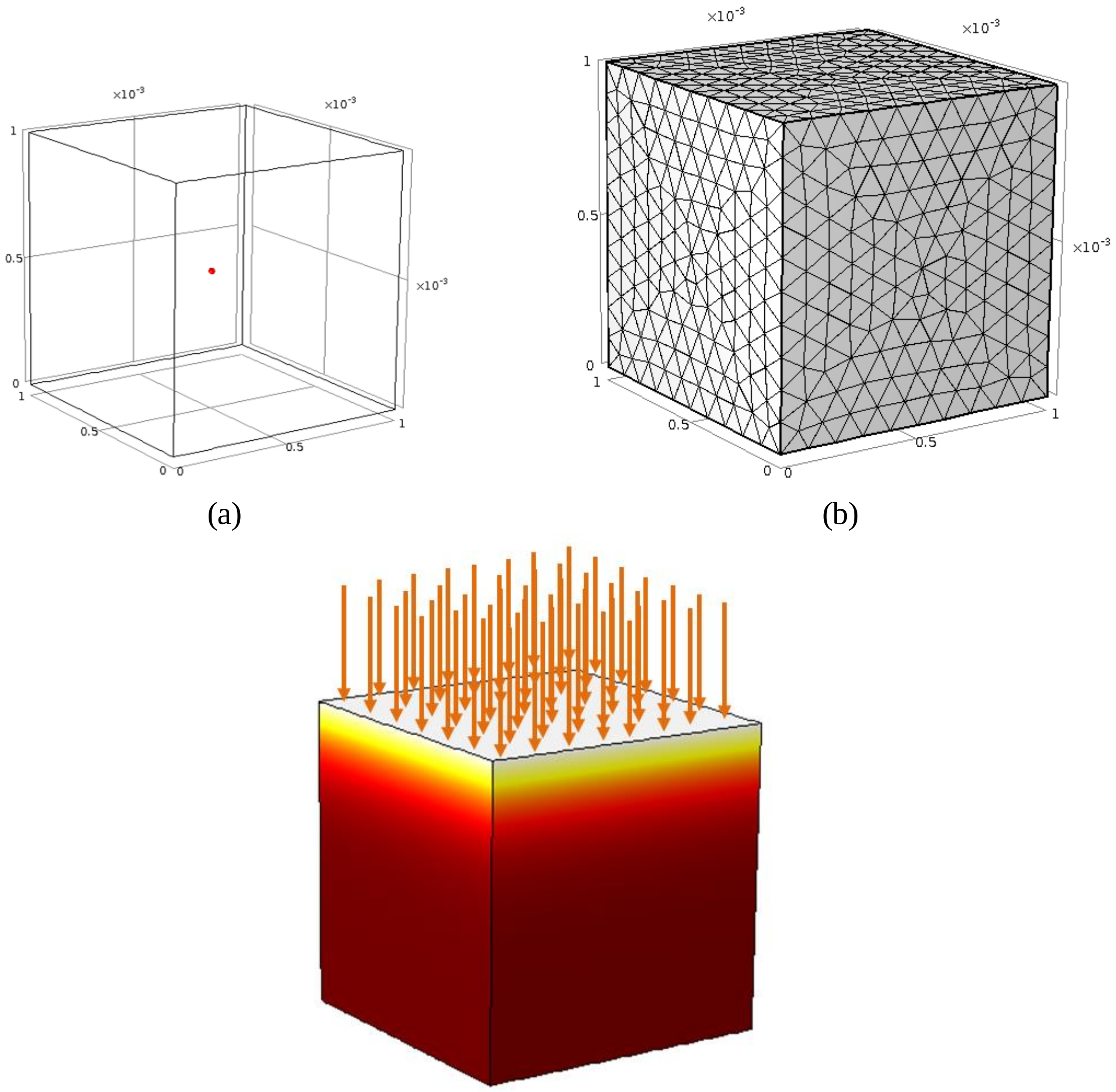


FIGURE 2 Schematic of variation of epoxy modified bitumen properties during isothermal chemical hardening



(a)

(b)

(c)

FIGURE 3 **Finite element cubic geometry: (a) location of output point in the centre of cube; (b) mesh and (c) direction of applied thermal field at the top boundary**

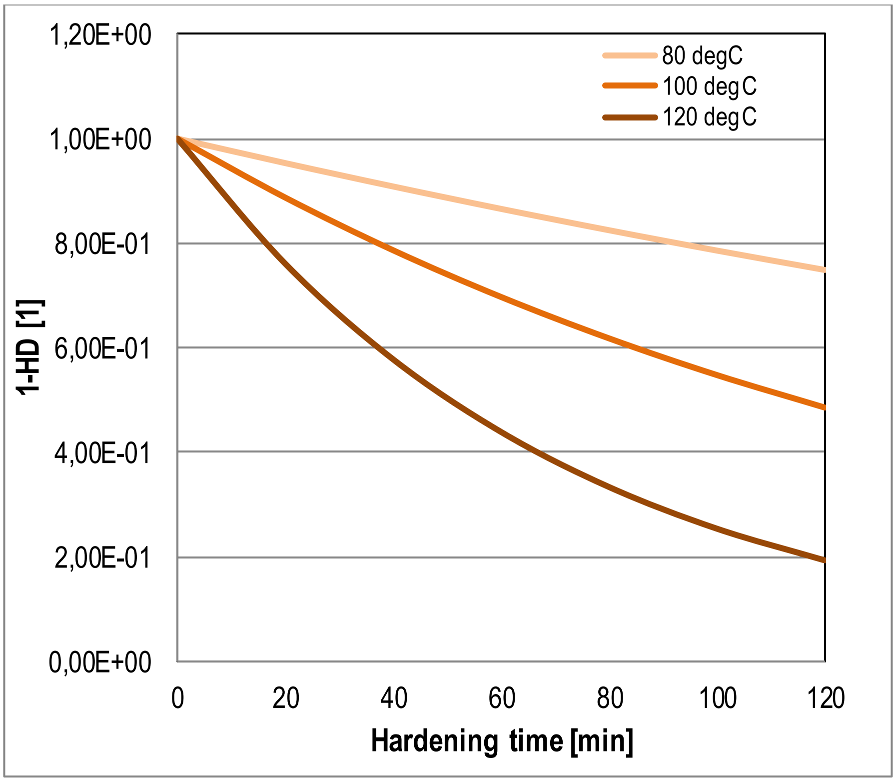
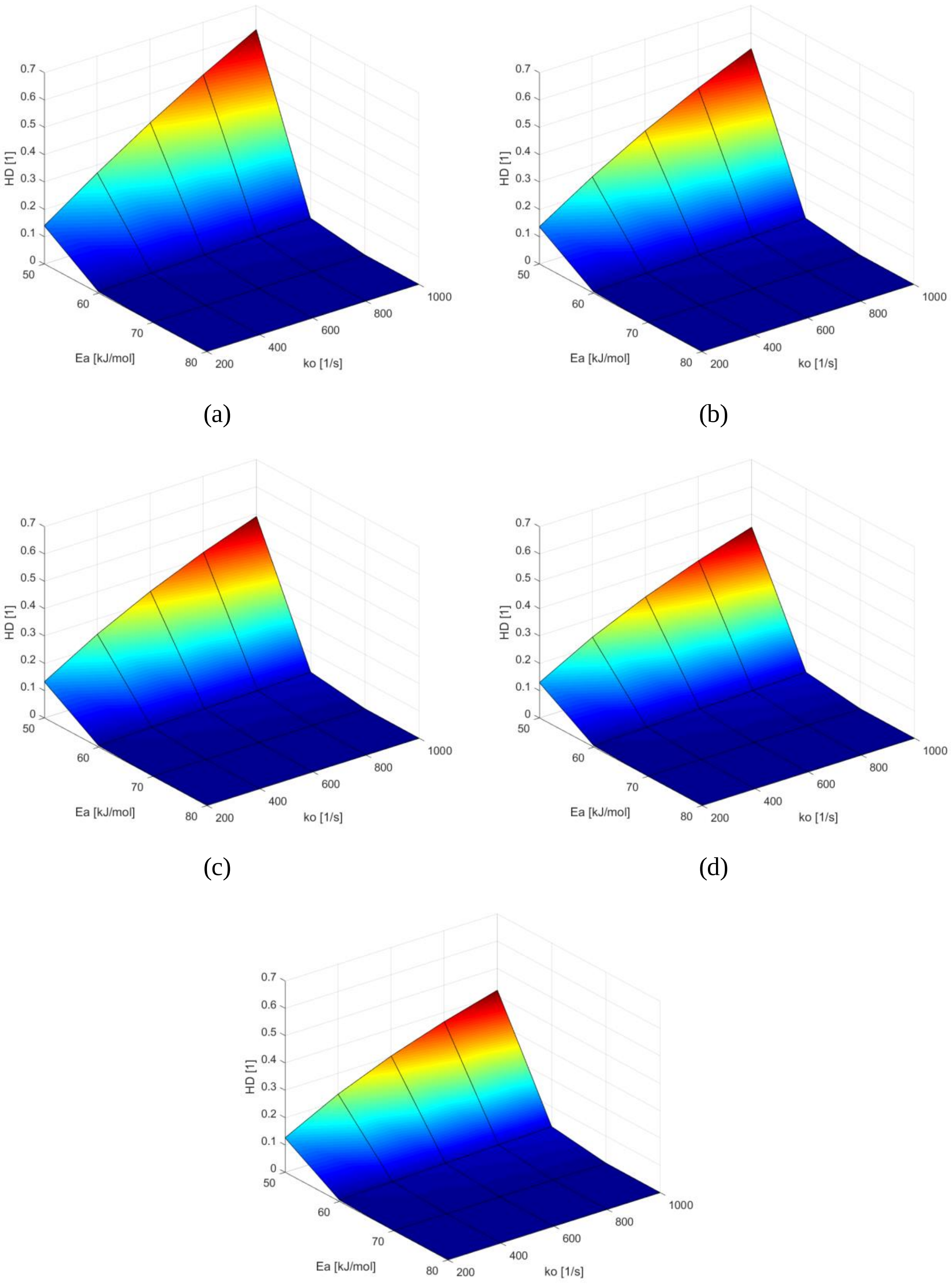


FIGURE 4 **Typical isothermal hardening of epoxy modified bitumen for different heating temperatures (E_a=50 kJ/mol, n=1, k_0=100 1/s)**

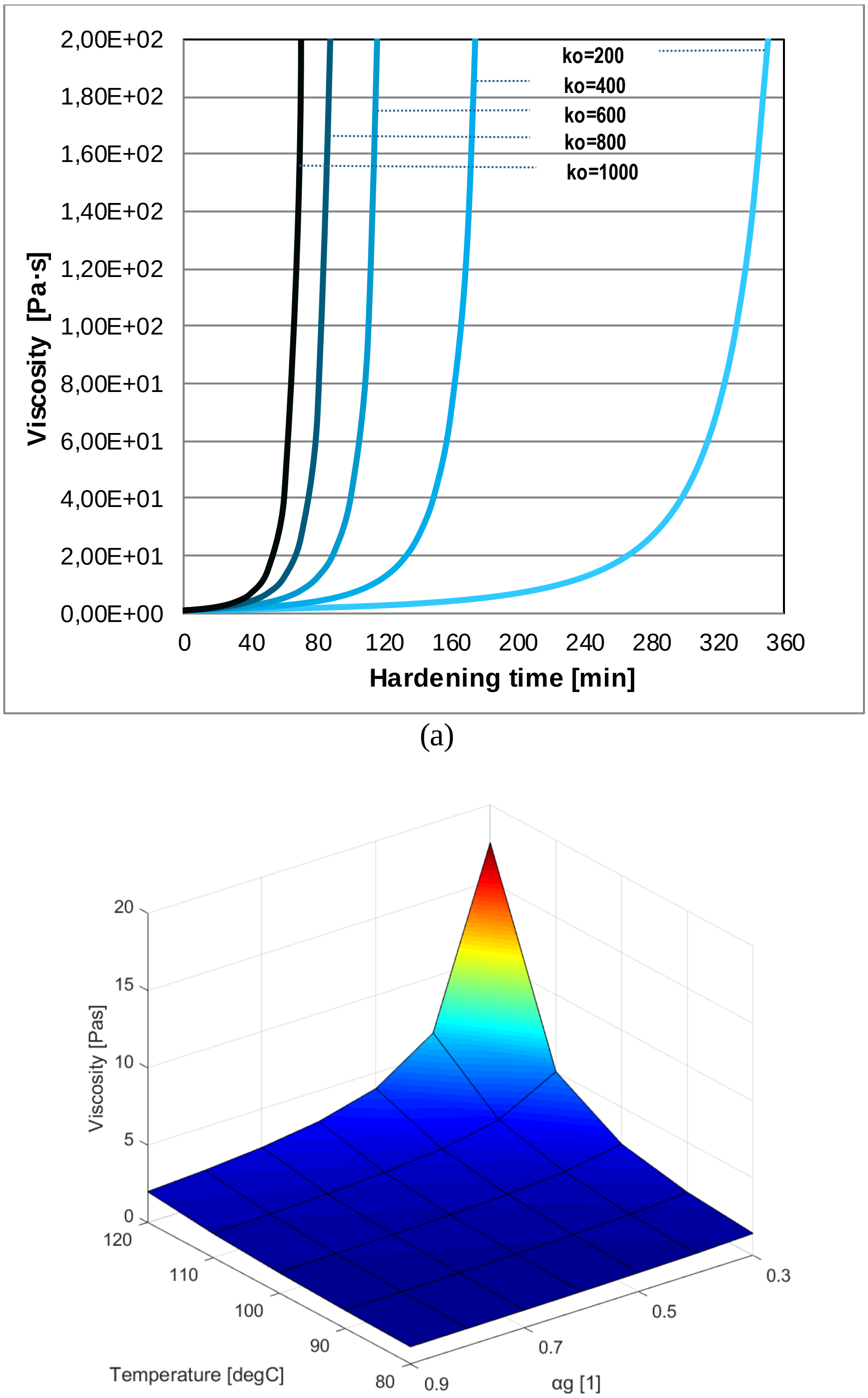


(a) (b)

(c) (d)

(e)

FIGURE 5 Variation of hardening degree for different activation energies and kinetic factors with reaction orders of (a) 0.4, (b) 0.8, (c) 1.2, (d) 1.6 and (e) 2.0 (T=100 ^{o}C and 120 min)



(a)

(b)

FIGURE 6 Predicted viscosity development of epoxy modified bitumen for : (a) different k_0 and (b) different α_g at various temperatures (Ea=50 kJ/mol, n=0.2, k_0=100 1/s)

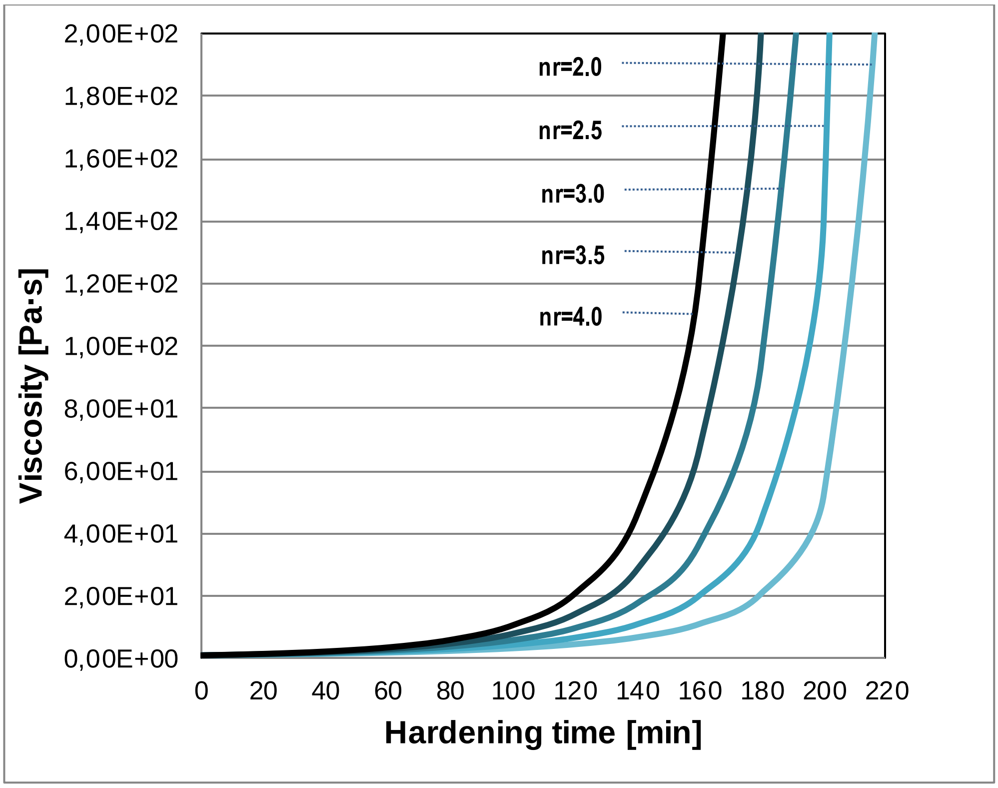
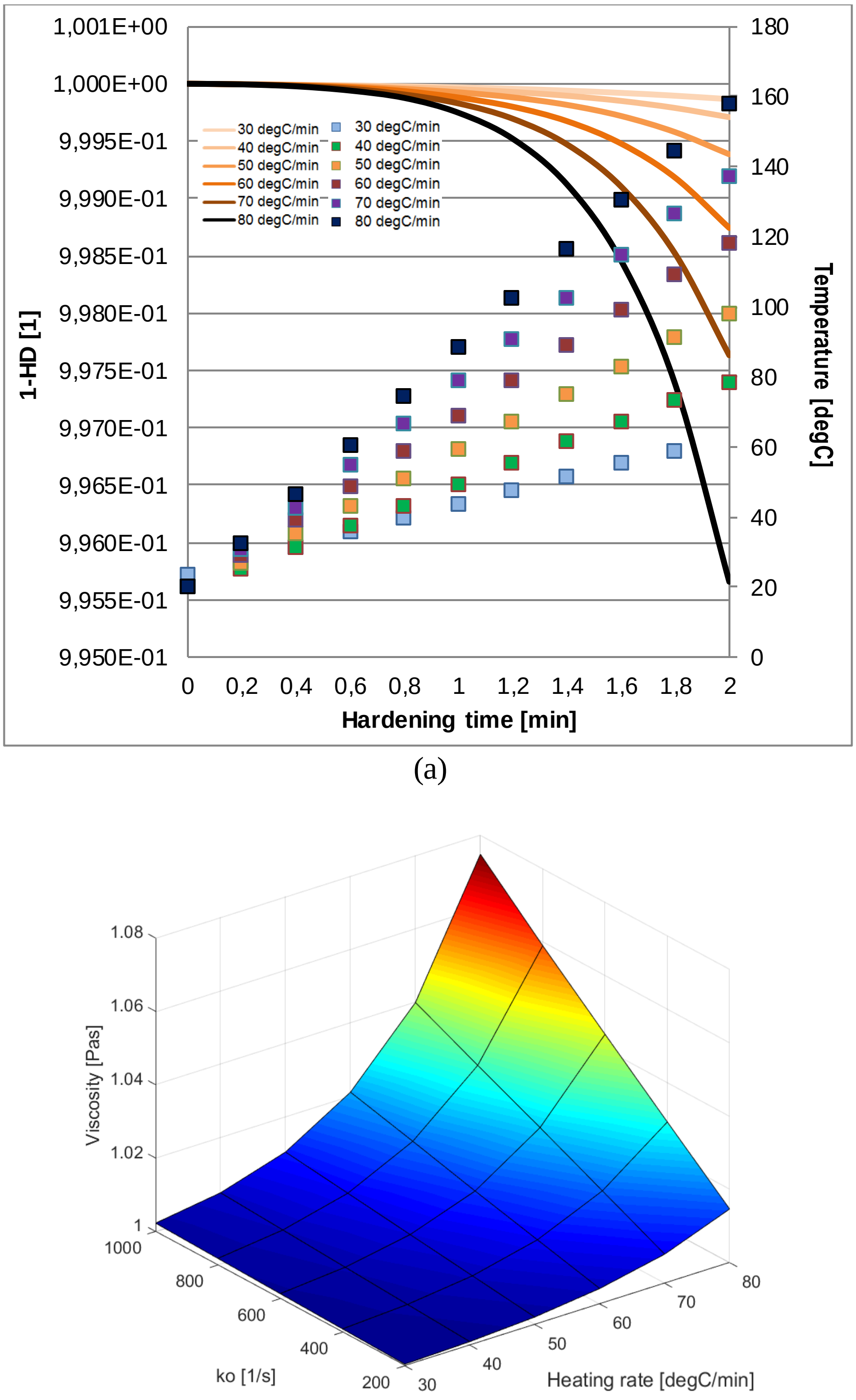


FIGURE 7 **Predicted viscosity development of epoxy modified bitumen under isothermal heating conditions for different n_r at T=100 ^{o}C (E_a=50 kJ/mol, n=0.2, k_0=100 1/s, α_g=0.6)**



(a)

(b)

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