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Induction hardening of thermoset modified bituminous materials

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ABSTRACT: Induction assisted chemical hardening (curing) or induction hardening is a novel in situ hardening technique for thermoset modified bituminous materials that maintains most of the advantages of natural chemical hardening while eliminating the possible restrictions of longer curing times at lower temperatures. In particular, induction heating can be utilized to accelerate the polymerization of thermoset modified bituminous paving mixes in which inductive particles are added. In this study, steel fibres are dispersed in a thermoset bituminous system and during exposure to an alternating magnetic field, they are induction heated leading to a more rapid initiation of the polymerization. The non-isothermal hardening performance of fast reacting thermoset-bitumen is modelled during the thermoset crosslinking. The model can also be utilized to predict reaction kinetics and viscosity evolution in this material, thereby indicating that induction hardening represents a reliable polymerization method and can be utilized to cure thermoset bituminous materials.

1 INTRODUCTION

The most widely used thermoplastic material in pavement constructions is bitumen. Because of the increasing demands for longer lasting paving materials, polymer modification of bituminous binders has become a solution. A remarkable durability improvement has been observed when thermoset polymer resins were blended with bituminous binders offering numerous advantages, such as superior stiffness and strength, fatigue resistance and oxidative aging resistance over conventional binders (Widyatmoko et al. 2006, Herrington and Alabaster 2008, Xiao et al. 2010). While the thermoset modification of bitumen has been introduced as a long lasting solution on orthotropic steel deck bridges since the 1970s, only recent studies have suggested the industrial transfer of this technology to pavements (International Transport Forum 2017). However, in these studies, it was mentioned that contractors could face high risks of failures during construction, because of the relatively slow chemical hardening (curing) of the binder during the early traffic period of the pavements. Thus, if feasible methods can be deployed to reach hardening rates comparable with normal techniques and quick in-situ hardening of thermoset modified bituminous (TMB) paving mixes, traffic can be allowed on the surface short after construction with significant savings in terms of energy consumption and gas emissions compared to normal bituminous mixes.

The proposed technology describes a supportive technique based on induction heating which can work as a catalyst to speed up the reactions of TMB mixes immediately after construction of the pave-

ment. This will provide a solution for pavements to be opened to traffic immediately after construction. Via this technology, the problem of uncontrolled hardening can be overcome and this will make the widespread use of thermosets in bituminous paving materials possible. However, induction heating has not previously been used to induce an in situ hardening of TMB mixes and there is not a model available developed to predict the material performance. Therefore, the main focus of this study is to enable the simulation of chemical hardening due to heating of steel fibres in TMB mixes. The hardening of TMBs due to crosslinking of linear pre-polymers and the network formation from monomers is a complex process that involves the continuous chemical alteration of its polymeric part and its chemical interaction with bitumen. To simulate the externally triggered hardening in TMBs, numerical analyses have been performed.

2 PROPOSED TECHNOLOGY

Apart from the hardeners of the TMB binders, the initiation of thermosets hardening into the bituminous matrix is triggered via external non-isothermal heating. The heat source is provided with electromagnetic induction to mixes causing temperature and reaction rate gradients. However, no hardening-induced heating techniques are available for paving materials. Issues like too slow reaction and limited polymerization can occur when the TMB system has no access to external heat sources especially when construction takes place at low temperatures.

In this study, the application of an induction heating technique is proposed to overcome the tempera-

ture restrictions during field operations and to control in-situ hardening. Induction heating as an assisting hardening technology has not been tried before in TMB mixes. It can be used as an external heating method to trigger indirectly the thermoset polymerization. The added inductive fibres are the only included components in the bituminous matrix responding to the supplied alternating magnetic field and they locally generate heat at the right place in the TMB system. Induction hardening maintains most of the advantages of efficient polymerization while being an environmentally friendly method that helps the hardening without the use of extra solvents, but with some extra energy cost. Furthermore, since the ultimate hardening extent is controlled by crosslinking the network rigidity of a thermoset-bitumen system, the hardener hardly can react further with thermoset monomers after gelation. Gelation of material is reached when the average molecular weight of polymers in bitumen and the material viscosity rises to infinity. Thus, another potential advantage of this induction hardening technology is that the hardener mobility may increase along with the applied alternating electromagnetic field and the hardener can interact more efficiently to crosslink a rigid network. All the above aspects make induction hardening a promising in situ polymerization method for thermoset modified bituminous paving mixes.

Induction heating has been used in the pavement industry in the last decade for paving mixes, mainly for healing of micro-cracks in bituminous mixes (Liu et al. 2012, Liu et al. 2013, Garcia et al. 2013, Apostolidis et al. 2016, Apostolidis et al. 2017). However, induction heating has been widely employed for a long time by embedding inductive particles in the thermoplastic matrices of composites to reach melting, welding, coating or adhesion. Such studies utilized induction heating as a source for heating polymers. Induction heating has not been previously utilized to improve in situ polymerization of TMB mixes and there has not been a fundamental framework developed for an in situ polymerization which combines both induction heating and chemical reaction kinetics. Therefore, a model has been developed, which describes the heating phenomenon through induction to activate polymerization of TMB and predict the material hardening mechanism.

3 THEORETICAL BACKGROUND

Once the resinous part reacts chemically with the hardener in the bituminous matrix, irreversible hardening is initiated by forming a three-dimensional resinous molecular network, which restricts the movement of bitumen molecules. Higher temperatures lead to higher exothermic polymerization reac-

tion rates and subsequently to higher viscosities before the gel point. The reaction rate of TMB systems is temperature-dependent and the hardening conversion is initiated via thermal heating. Hence, the ability of the TMB system to harden in situ within sufficient time under very low temperature conditions is improved. The proposed induction hardening accelerates the polymerization of the studied material directly after construction and enhances the material polymerization beyond the current state-of-the-art enabling quick opening of the road to traffic. Based on this new specific technology, a model of in situ polymerization triggered by heating was developed to predict the viscosity evolution of TMB. The governing equations are given in the following subsections, but a detailed description is presented elsewhere (Apostolidis et al. 2018).

3.1 Hardening kinetics governing equations

The determination of the TMB reaction kinetics is crucial to be able to apply the viscosity prediction scheme since the evolution of material viscosity depends on the hardening degree. In this case, the reaction process is assumed as one step n -th order exothermic reaction and the kinetics model before the material gelation is given as

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

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

3.2 Heat transfer governing equation

In TMBs, the start of the crosslinking process is driven by external heat and, for this reason, the utilization of induction heating is so important. The governing equation of the transient heat conduction within the hardening TMB is described by Eq. 2

$$\rho c_p \nabla T - \nabla \cdot (k \nabla T) = \rho \Delta H_{exo} \frac{\partial \alpha}{\partial t} \quad (2)$$

where ρ is the mass density of the TMB system, k denotes the thermal conductivity, c_p is the heat capacity, T is the temperature, ΔH_{exo} is the polymerization enthalpy (kW/m^3). For simplicity reasons it was among others assumed that the convection and radiation heat do not have an important impact on the energy balance of the system and, in case of hav-

ing the assistance of induction heating, the temperature T increases in the interfacial surfaces between steel fibres and mastic. As the resin turns into a networked microstructure and the TMB hardens, heat is released, which is proportional to the consumption rate of reactive elements in the TMB system.

3.3 Chemo-rheological governing equation

In case of thermosets, the material transformation takes place when the resin is liquid of low molecular weight and alters to a rigid solid of infinite polymeric network without any molecular movement. This transformation happens when the gelation point is reached and is triggered by a significant increase of the viscosity. Extensive research has been conducted to determine the appropriate models to simulate the time-dependent chemo-rheological thermoset performance. A modified William-Landel-Ferry equation (Castro and Macosco 1980) describes the chemo-rheology of TMB as

$$\eta^*(T, \alpha) = \eta_g^* \cdot \exp\left[-\frac{C_1(T-T_g)}{C_2+T-T_g}\right] \cdot \left(\frac{\alpha_g}{\alpha_g-\alpha}\right)^{n_r} \quad (3)$$

where α_g is the extent of reaction at the gel point, T_g is the glass transition temperature, η_g^* is the complex viscosity at the glass transition temperature, C_1 and C_2 are material-dependent and temperature-independent and n_r is a material-dependent constant.

4 FINITE ELEMENT SIMULATION

By adding inductive fibres, a TMB system can be heated and hardened in short time by using induction technology. To simulate the heating induced hardening of a fast reacting inductive TMB (inTMB) with steel fibres, a micro-mechanical 3D finite element mesh of 502E3 elements was generated (Figure 1) by post-processing computed tomography scans of mix with steel fibers (Figure 2) (Apostolidis et al. 2016). For the analyses, the mesh was directly imported into COMSOL Multiphysics. The input material parameters were determined elsewhere (Apostolidis et al. 2016). Since the studied material considered very reactive (Yang et al., 1999, Prime et al. 2005), reaction order of 5E3 1/s and activation energy of 4E1 kJ/mol were assumed. Moreover, the gelation of the system occurred at a fixed hardening degree (HD) (e.g., $\alpha_{gel}=6E-1$). The viscosity at the glass transition temperature was assumed to be 1E-2 Pa·s and various implied non-isothermal heat fields were defined at the interfacial boundaries between fibres and thermoset bituminous part, with the rest of the boundaries to be thermally insulated. Figure 3 shows the contour plot of temperatures developed

after 2 minutes of heating the thermoset bituminous part with 6E-1 °C/sec rate.

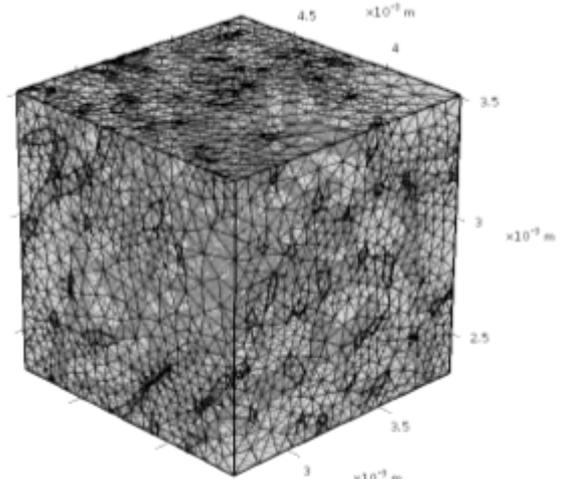


Figure 1. FEM mesh of inTMB reconstructed by CT-scans

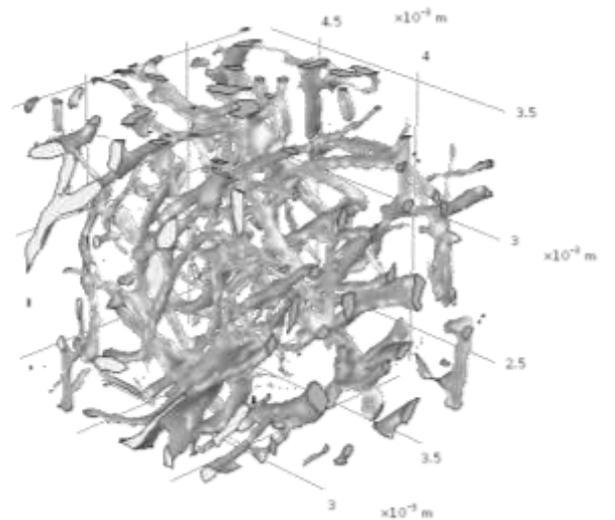


Figure 2. Steel fibers distribution in inTMB

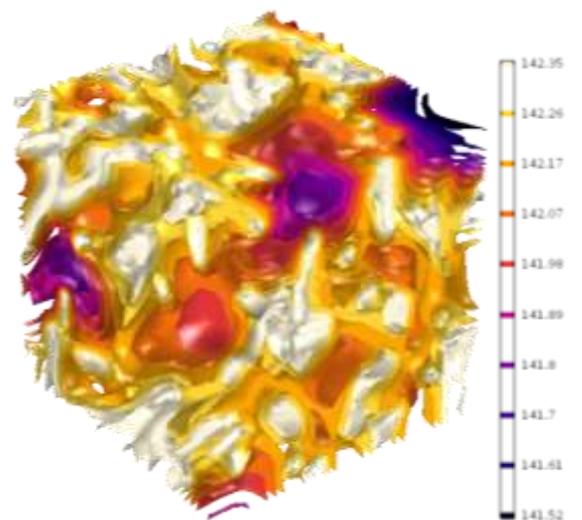


Figure 3. Iso-surface temperature of inTMB at 2 minutes

5 RESULTS

The current model has been developed to demonstrate now the concept works of induction hardening in thermoset modified bituminous materials by

simulating the non-isothermal material polymerization. However, it should be mentioned that the effects of heating on the hardening of a thermoset also depend on the particular hardening agent used, but for this example is not taken into account. Figure 4 shows the HD and viscosity evolution over time for an inTMB system when heating rates are varied. Significant increase in the rate and extend of chemical reaction can be seen for the inTMB system at higher heating rates due to the acceleration of cross-linking via electromagnetic induction. Furthermore, the crosslinking reaction has been enhanced by increasing the heating rate. Faster polymerization during in situ induction hardening of bituminous mixes will be possible when higher heating rates, and thus higher applied induction energy, are generated. The thermoset molecular magnetic field interaction is not considered in this model. However, electromagnetic induction could heat up these molecules directly because of the relaxation of molecular dipoles polarization along the applied field. This provides a new function of this technology in polymerizing thermoset bituminous materials and could speed up the chemical hardening even more and should be considered for future research.

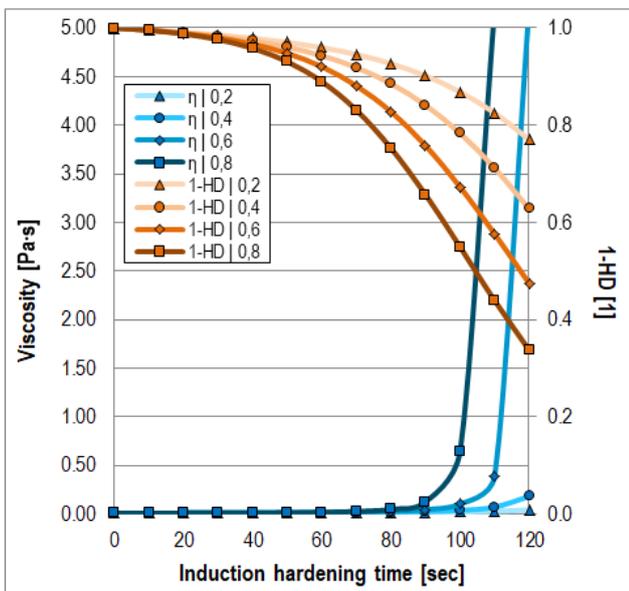


Figure 4. Non-isothermal induction hardening of inTMB

6 CONCLUSIONS

The use of electromagnetic induction technology to catalyse the polymerization of thermoset bituminous materials with steel fibres has been proposed in this paper. The heating due to electromagnetic induction can stimulate the hardening of the modified bitumen providing the opportunity for faster mechanical properties development before opening the pavement to traffic. In the field application of this technique, an induction coil equipped in a vehicle can

pass to heat up the TMB layer and accelerate in this way the material polymerization process. The induction assisted catalysis of the thermoset hardening process within the inductive bituminous mix might be performed as a single-pass or multi-pass operation.

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