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Dissolution simulation of polymers in bitumen

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ABSTRACT: Fundamental models should be developed and utilized in order to facilitate the chemo-mechanical design of modified binder systems for paving applications but not only. Especially, the fact that the incorporation of new chemical substances used as bio-based modifiers or alternative binders is attracting great interest to replace traditional technologies, the development of tools able to provide insight into the various physio-chemical phenomena is crucial. Among other polymer-bitumen interaction phenomena, the dissolution mechanism of polymers in bitumen is a significant aspect that should be considering in order to enhance binder properties through polymer modification. The current research gives emphasis on modelling the mechanism of dissolution for rubbery polymers in bitumen.

1. INTRODUCTION

Building fundamental tools and insights into the chemo-mechanical design of polymer-bitumen systems remains crucial in the field of asphalt chemistry. Bio-based modifiers provide a unique opportunity for replacing petroleum derived chemicals in pavement systems and their success depends on selecting the suitable bitumen and polymers in order the latter to be disentangled at the desired rate and extent over time. For instance, lignin or bio-based waxes are naturally occurring glassy or crystal-like polymers with unique functionalities when they are dissolved in bitumen.

An appropriate understanding of the various controlling steps in the dissolution process is needed to tailor the bitumen modification techniques, especially when semi-crystalline or glassy bio-based polymers are incorporating in bitumen. Moreover, the control of disentanglement rate of polymeric chains in binders used for paving applications is associated with thermodynamics changes. Thus, the knowledge of the dissolution behaviour of certain polymers will enable material designers to develop well-dissolved modified binders of desired micro-structural and morphological features and ultimately mechanical properties. Herein, in order to provide guidance for the selection of suitable bitumen through the polymer modification, the dissolution mechanism of glassy polymers in binders is introduced and assessed as well by performing numerical simulations.

2. BACKGROUND

The mechanism of polymer dissolution into a solvent, such as bitumen, involves two phenomena; solvent diffusion and chain disentanglement. Once a polymer is in contact with a miscible solvent, species of the latter diffuses into the polymer and a gel-like layer is formed adjacent to the solvent-polymer interface due to the solvent induced-plasticization of polymer (Wang et al. 2019, Wang et al. 2020a, Wang et al. 2020b). Once semi-crystalline polymers are exposed to miscible solvents, unfolding of the crystalline regions is an additional step accompanying solvent diffusion and chain disentanglement. Hence, semi-crystalline polymer dissolution becomes equivalent to amorphous polymer dissolution after unfolding the crystals in polymer.

The polymer dissolution differs from dissolution of a non-polymeric material. Polymers require a time period before starting to dissolve, while non-polymeric materials dissolve instantaneously. Also, polymer dissolution can be controlled either by the disentanglement of the polymer chains or by chains diffusion through a boundary layer adjacent to the solvent-polymer interface. Moreover, swelling occurs and the polymer begins to release its contents to the surrounding solvent, either via solute diffusion or polymer dissolution, and hence, certain solvents exhibit an altered dissolution rate of the exposed areas of polymers.

The entanglement process of glass polymers has been extensively assessed via modelling the

concentration of acting species at polymer-liquid interface (Papanu et al. 1989) and the polymeric thickness (Lee and Peppas 1987, Peppas et al. 1994, Devotta et al., 1994a, 1994b) changes over time. Disentanglement kinetics related to the swelling rate have been modelled as well predicting thus the changing mobility of the disengaging macromolecule at the gel-liquid interface (Devotta et al., 1995). In this research, special emphasis was given on modelling the transport phenomena at the gel-liquid interface.

3. MUTUAL DIFFUSE-REACTION MODEL

As the solvent penetrates into the polymeric film, the solvent species diffuses into the material, the thickness of the latter may increase (swelling) depending on the nature of polymer, and a gel phase is formed at the polymer-solvent interface. Simultaneously, the polymeric chains at the gel-liquid interface disentangle themselves (see **Fig. 1**). If the size of diffusing species of solvent is small, then the latter penetrates into the polymer quickly. Thus, the mobility of the gel-like chain increases faster (high diffusivity) and such highly mobile chains disengage at the gel-liquid interface rapidly.

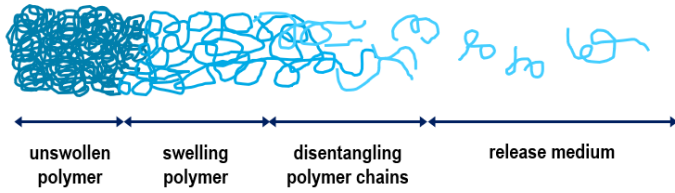


Figure 1. Polymer dissolution process.

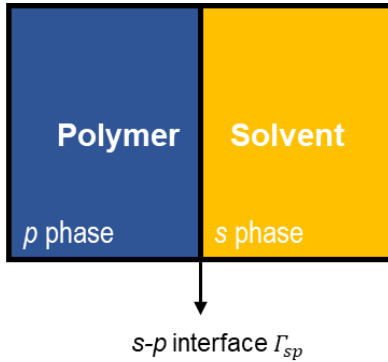


Figure 2. Schematic representation of the polymer and solvent phases.

By assuming the physical entanglement in the gel phase to chemical crosslinks, the chemical driving force of mutual diffusion process is determined by the chemical potential difference for the species of interacting phases p (polymer) and s (solvent) at the s - p interface (see **Fig. 2**) and expressed as

$$\Delta G_m = \sum_i^n \varphi_i^0 [\mu_{is}(\varphi_{is}^{\Gamma sp}) - \mu_{ip}(\varphi_{ip}^{\Gamma sp})] \quad (1)$$

where φ_i^0 is the concentration of interacting species (i) transferred over the interface, n is the number of different interacting species (P and S), $\varphi_{is}^{\Gamma sp}$ and $\varphi_{ip}^{\Gamma sp}$ are the molecular fractions of interacting species of s and p phases at the s - p interface (denoted as Γ_{sp}), respectively, μ_{is} and μ_{ip} are the chemical potentials of the i^{th} species in s and p phases.

In thermodynamic equilibrium, the chemical potential of solvent and polymeric species is equal at Γ_{sp} and it is expressed as

$$\mu_{Ps}(\varphi_{Ps}, T, p) = \mu_{Pp}(\varphi_{Pp}, T, p) \text{ at } \Gamma_{sp} \quad (2)$$

In the complete binary case ($\varphi_{Ps} \neq 1$), there is also a relation similar to **Eq. 2** for the other component.

For the case under consideration, both solvent phase and polymer phase are immobile. The mass balance equations for species P and S in the solvent phase are

$$\frac{\partial(\rho_s \varphi_{Ps})}{\partial t} - \nabla \cdot (\rho_s D_{Ps} \nabla \varphi_{Ps}) = 0 \quad (3)$$

$$\frac{\partial(\rho_s \varphi_{Ss})}{\partial t} - \nabla \cdot (\rho_s D_{Ss} \nabla \varphi_{Ss}) = 0 \quad (4)$$

where ρ_s is the density of solvent; D_{Ps} is the liquid binary diffusion coefficient; D_{Ss} is the self-diffusion coefficient of solvent.

The mutual diffuse-reaction process is controlled by thermodynamic equilibrium at the interface and is translated into a simple Dirichlet condition. Therefore, an equilibrium concentration for species P at the polymer-solvent interface is expressed as

$$\varphi_{Ps} = \varphi_{eq} \text{ at } \Gamma_{sp} \quad (5)$$

The mass balance equation for species P and S at the s - p interface gives

$$(\rho_s D_{Ps} \nabla \varphi_{Ps}) \cdot \mathbf{n}_{sp} = (\rho_p \varphi_{Pp} \mathbf{w}) \cdot \mathbf{n}_{sp} \text{ at } \Gamma_{sp} \quad (7)$$

$$(\rho_s D_{Ss} \nabla \varphi_{Ss}) \cdot \mathbf{n}_{sp} = (\rho_p \varphi_{Sp} \mathbf{w}) \cdot \mathbf{n}_{sp} \text{ at } \Gamma_{sp} \quad (8)$$

The total mass balance at the s - p interface gives

$$\rho_s \mathbf{w} \cdot \mathbf{n}_{sp} = \rho_p \mathbf{w} \cdot \mathbf{n}_{sp} \text{ at } \Gamma_{sp} \quad (9)$$

where \mathbf{w} is the velocity of the s - p interface. The whole balance equations presented above are sufficient to solve the physical problem, provided

that the overall surrounding boundary conditions are given as

$$\mathbf{n}_{sp} \cdot \mathbf{w} = \mathbf{n}_{sp} \cdot \left(\frac{\rho_s}{\rho_p(1-\varphi_{Ps})} D_{Ps} \nabla \varphi_{Ps} \right) \quad (10)$$

at Γ_{sp}

$$0 = \mathbf{n}_{sp} \cdot \left(\frac{\rho_s - \rho_p}{\rho_p(1-\varphi_{Ps})} D_{Ps} \nabla \varphi_{Ps} \right) \quad (11)$$

at Γ_{sp}

All the above expressions give the recession velocity and the s -phase velocity at the interface, which are necessary to implement the direct explicit numerical methods.

3 FINITE ELEMENT SIMULATIONS

The two-dimensional (2D) polymer dissolution in bitumen at 100 °C was simulated herein by implementing the above described concurrent mutual diffuse-reaction model in a commercially available multi-physics tool. 2D mesh is demonstrated in **Fig. 3** where the blue part represents the polymer surrounding with the solvent. The disentanglement rate and the activation energy were selected as 2000 1/s and 30 kJ/mol at 100 °C. The diffusion coefficient assumed constant as $1e-13$ m²/s ($D_{Ps} = D_{Sp}$), with the initial concentration of interacting species to be equal as 0.001 mol/m³ ($\varphi_{Ps} = \varphi_{Ss} = \varphi_{Pp} = \varphi_{Sp}$).

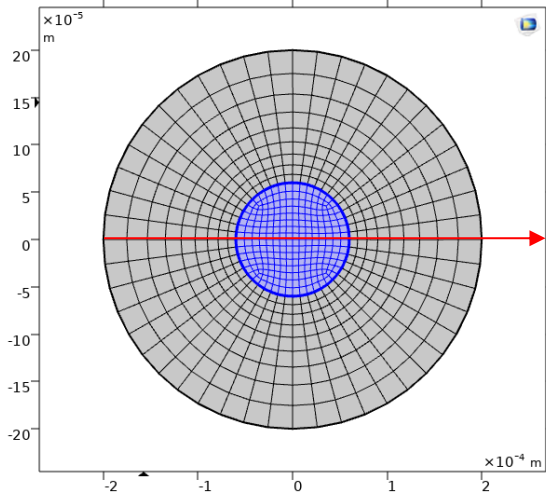


Figure 3. Finite element geometry and mesh (number of quad elements: 240 and 430 for polymer and solvent, respectively)

Fig. 4a and **4b** show the general prediction of the variation of surface concentration of the polymeric and dissolved species in the domains of both polymer and solvent phases after the diffusion and disentanglement, respectively. In particular, **Fig. 4a** clearly demonstrates the continuous decrease of polymeric species concentration from the centre of polymer phase to solvent. From **Fig. 4b**, it can be

found the polymer-solvent interface zone shows higher concentration of dissolved species.

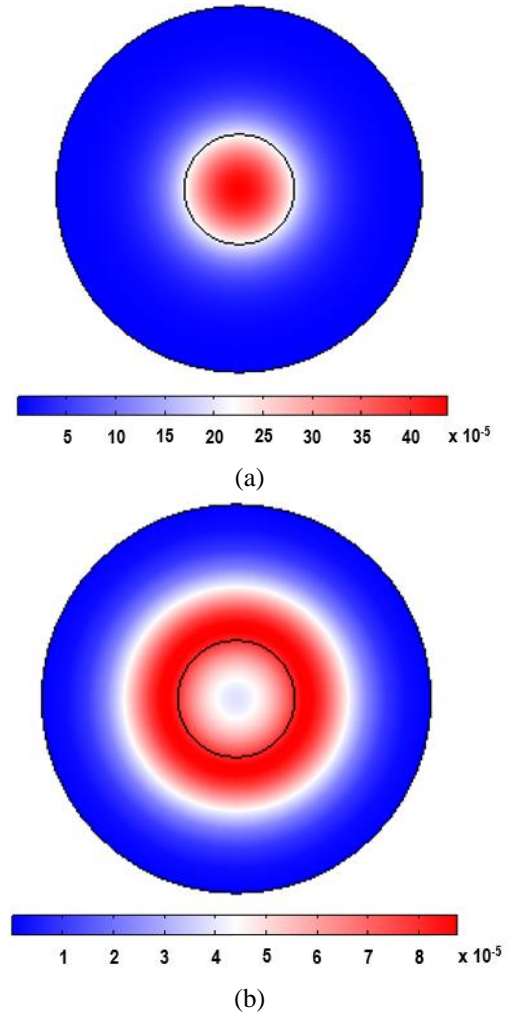


Figure 4. Predicted surface concentrations of (a) polymeric species and (b) dissolved species after diffusion disentanglement.

To further investigate the concentration profile, the concentration of dissolved species along the horizontal axis (shown as the red line in **Fig. 3**) over time is plot in **Fig. 5**. Obviously, the highest concentration of dissolved species is formed at the polymer-solvent interface where abundant polymer and solvent species are available to react resulting in the highest reaction/dissolution rate. Toward the inner layer of polymer phase, the concentration decreases. In solvent, similar phenomenon is observed at the locations away from the interface. This is due to lack of either polymeric or solvent species. As reaction proceeds, more and more polymeric species are dissolved into solvent and the dissolved species diffuse to the surrounding space, causing an overall concentration increase of dissolved species.

Fig. 6 summarizes the concentrations of solvent, polymer and dissolved species in the polymer phase at the s - p interface over time. It is apparent that the concentration of solvent species gradually decreases while the concentration of

dissolved species gradually increases as reaction proceeds. However, for the polymeric species in the solvent, it first increases due to the diffusion from the polymer phase and then, their concentration starts decreasing. The dissolution rate is higher than the diffusion rate, which enables the continuous decrease of the amount of polymeric species. The dissolution rate of polymer increases with increased amount of solvent species until a maximum rate is reached. After reaching a maximum, the dissolution rate decreases resulting in reduced swelling.

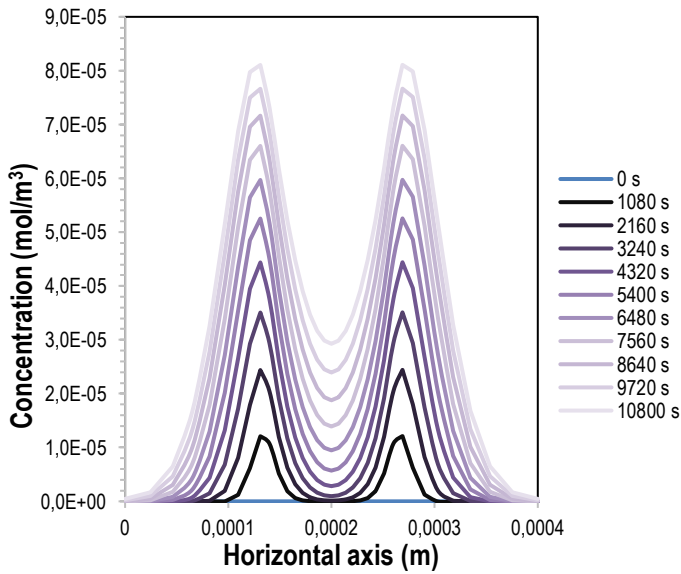


Figure 5. Predicted variation of concentration of dissolved species along the horizontal axis over time.

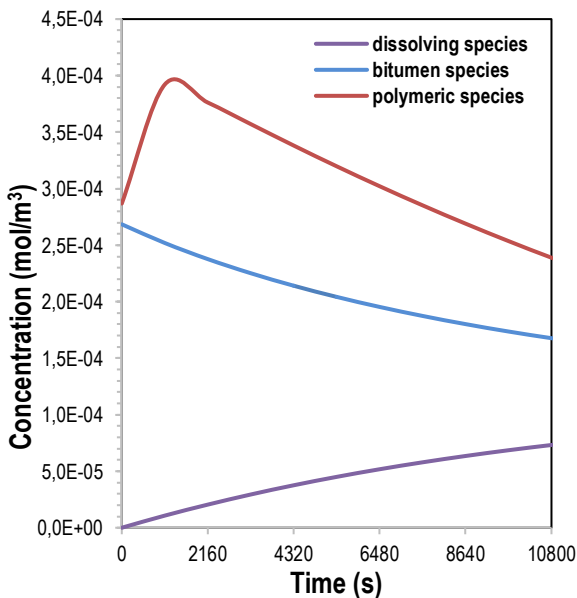


Figure 6. Predicted variation of concentration of solvent, polymer and dissolved species in the dissolution medium at the *s-p* interface over time.

4 CONCLUSIONS

The polymer-bitumen interaction plays critical role in controlling the properties of polymer modified binders. At high temperatures, the polymer-bitumen interaction is a polymer dissolution

process, which consists of swelling and chain disentanglement, and a degradation process. Full control of dissolving species in bitumen will help on obtaining the desired micro-structural and morphological features and subsequently the goal mechanical properties. In this study, emphasis was given on modeling the mechanism of dissolution, and particularly of chain disentanglement, of an already swollen polymer in solvent, or bitumen. Predictions on mass transport of reacting species are provided assisting on understanding the controlling thermodynamic parameters of polymer-bitumen interaction phenomena at micro-scale.

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