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Citation for the original published paper (version of record):

Zhu, J., Balieu, R., Lu, X., Kringos, N. (2017)

Numerical Prediction of Storage Stability of Polymer-Modified Bitumen: A Coupled Model of Gravity-Driven Flow and Diffusion.

Transportation Research Record, 2632: 70-78

<https://doi.org/10.3141/2632-08>

Access to the published version may require subscription.

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Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:kth:diva-195088>

Numerical Prediction of Storage Stability of Polymer-Modified Bitumen

A Coupled Model of Gravity-Driven Flow and Diffusion

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Word count: 5,058 words text + 8 tables/figures x 250 words (each) = 7,058 words

TRR Paper number: 17-01328

Submission Date: February 28, 2017

ABSTRACT

Aiming to predict the storage stability of polymer-modified bitumen (PMB), a coupled diffusion-flow model by phase-field method is proposed in this paper. The incompressible Navier-Stokes equations are coupled with a previously developed phase-field model for PMB phase separation. The coupled model has been implemented in a finite element software package with experimentally calibrated parameters and reported data in the literature. Effects of the affecting parameters (bitumen density and dynamic viscosity) on the gravity-driven flow and phase separation in PMB are evaluated at 180 °C with the simulation results. The results indicate that the coupled diffusion-flow model is capable of predicting storage stability (and instability) of PMBs. A good correlation between the simulation results and the previously reported experimental results (storage stability tube test) has been observed. The different gravity-driven phase separation behaviours of PMBs may result from the different composition of the equilibrium phases in the PMBs as well as the different densities and dynamic viscosities of the individual components (polymer and bitumen). A bigger polymer-bitumen density difference and/or a lower bitumen dynamic viscosity cause a faster flow and separation in the PMB at storage temperature. The investigated variation of bitumen dynamic viscosity has a more significant influence than the investigated variation of bitumen density in this paper, but this might depend on the specific values of the model parameters. With this study as a foundation, further experimental and numerical studies will be conducted towards storage-stable PMB binders and a more efficient test method for determining PMB storage stability.

KEYWORDS: Polymer-modified bitumen; Storage stability; Phase separation; Phase-field modelling; Navier-Stokes equations

INTRODUCTION

Polymer modification is an effective way to improve the properties of paving bitumen to some extent. Polymer-modified bitumen (PMB) has been widely used in road construction and maintenance in many countries. But some fundamental aspects related to the polymer modification of paving bitumen are still not fully understood today (1, 2), which may limit the sustainable application of PMB. One of the identified common issues for PMB is the potential storage instability problem (3-7). With a poor compatibility and big density difference between the polymer modifier and bitumen, the PMB may show instability during the storage and transport, i.e. the separation of the polymer-rich phase from the bitumen-rich phase.

This phase separation process is controlled by many factors. Diffusion and flow may be the main mass transfer modes in this process (8). Some previous studies (9-12) have indicated that the influence of gravity due to the polymer-bitumen density difference is one of the causes for PMB phase separation in the vertical direction. However, the gravity effect might not be the direct cause for the separation but could just accelerate the possible phase separation process in the vertical direction (13). This means that an unstable PMB starts to separate into two phases by diffusion, because of the poor polymer-bitumen compatibility. Once the density difference between the two phases becomes sufficiently significant, gravity starts to drive the flow of the two phases and accelerate the separation in the vertical direction.

In order to investigate such a coupled diffusion-flow process, a numerical approach through a simplified system may provide a convenient way for a fast identification of the affecting parameters and a preliminary evaluation on their influences beforehand of the experimental study. The authors have developed a phase-field model (8) for describing and predicting PMB storage stability and phase separation behaviour. However, the model in (8) demonstrates only the diffusion process related to the PMB phase separation. On the basis of this diffusion model, this paper aims to present a coupled diffusion-flow model and simulate the gravity-driven flow in PMB at the storage temperature. For this, the Navier-Stokes equations are coupled with the diffusion model. After the modelling, effects of the model parameters are evaluated with simulation results, which can provide the necessary information for further experimental and numerical investigations. The results of this research are expected to be helpful for understanding the impact of gravity-driven flow on PMB phase separation and contribute to knowledge that can lead to identify the potential causes for PMB instability, find the solutions and eventually prevent the storage instability problem from occurring.

PHASE-FIELD MODELLING FOR GRAVITY-DRIVEN FLOW IN PMB

A Phase-Field Model for PMB Phase Separation

Considering PMB as a pseudo-binary blend, a phase-field model has been proposed in (8) for demonstrating the diffusion process related to the PMB phase separation at storage temperature. In this diffusion model, the phase-field variable is the local volume fraction of the polymer modifier in PMB. It is a conserved phase-field variable and its evolution is governed by the Cahn-Hilliard equation (14), i.e.

$$\frac{\partial \phi}{\partial t} = \nabla \cdot M(\phi) \nabla \frac{\delta F}{\delta \phi}, \quad (1)$$

where ϕ is the local volume fraction of the polymer modifier in PMB; t is time; ∇ is the Nabla operator; $M(\phi)$ is the mobility coefficient of the phase; and F is the free energy of the PMB system. This model uses a composition-dependent mobility coefficient, which means that the mobility coefficient of the phase depends on the local composition of the phase as well as the mobility coefficients of the individual components (polymer and bitumen). Under the incompressible condition, a linear dependency is postulated in the model, such that

$$M(\phi) = M_p \phi + M_b(1 - \phi), \quad (2)$$

where M_p is the mobility coefficient of the polymer modifier; and M_b is the mobility coefficient of the bitumen.

Since no coherent microstructure is formed in the paving PMB at the high temperatures for storage and transport, no long-range free energy (e.g. elastic energy, electrostatic energy and magnetic energy) is involved in this case (15). Thus, the free energy term F for PMB system in the model consists of the free energy of pure components (polymer and bitumen), the free energy change due to mixing them and the gradient energy. Using a common expression for the gradient energy density, the total free energy F is formulated as

$$F = \int_V (f_0 + \Delta f_m + \frac{1}{2} \kappa |\nabla \phi|^2) dV, \quad (3)$$

where V is the volume of the considered body; f_0 is the free energy density of the pure components (sum of polymer and bitumen); Δf_m is the free energy density change due to mixing; and κ is the gradient energy coefficient. The sum of f_0 and Δf_m represents the local contribution to the free energy, named as the local free energy. For a given PMB, f_0 is dependent on the temperature and does not affect the minimization of the total free energy at a fixed temperature. In this model, Δf_m is expressed by a modified form of the Flory-Huggins free energy of mixing, with some simplifying assumptions made according to the fact that bitumen is a complex mixture of various molecules, such that

$$\Delta f_m = RT \left[\frac{z\phi}{N_p} \ln(z\phi) + \frac{1-z\phi}{N_b} \ln(1 - z\phi) + z\phi(1 - z\phi)\chi \right], \quad (4)$$

where R is the universal gas constant; T is the temperature; z is the dilution parameter; N_p is the segment number of the polymer chains in the Flory-Huggins lattice; N_b is the segment number of the hypothetical chains for bitumen in the Flory-Huggins lattice; and χ is the interaction parameter between polymer and the hypothetical chain for bitumen. In Equation 4, N_p and N_b characterize the molecular size (and its distribution for bitumen) of the polymer and bitumen; χ characterizes the degree of the polymer-bitumen interaction; and z characterizes the relative amount of interactive molecules in the bitumen. More details about the model can be found in (8).

Coupling with Navier-Stokes Equations

In order to simulate the gravity-driven flow in PMB at the storage temperature, the incompressible Navier-Stokes equations are coupled with the above formulated diffusion model. Since the discussed temperature is fixed in this paper, the governing equations include only the mass and momentum conservation equations (not the energy conservation equation). Under the incompressible condition, the continuity equation in vector notation has the form of

$$\nabla \cdot \mathbf{u} = 0, \quad (5)$$

where $\mathbf{u}$ is the velocity vector. As this paper is considering a two-dimensional model, the velocity is a two-component vector as $\mathbf{u} = (u, v)$. The equations of motion in vector notation can be written as

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla p + \mu \nabla^2 \mathbf{u} + \mathbf{F}, \quad (6)$$

where ρ is the density; p is the pressure; μ is the dynamic viscosity; ∇^2 is the Laplace operator; and $\mathbf{F}$ is the force vector. The force term $\mathbf{F}$ can represent gravity, surface tension and/or other external forces. In this paper, only gravity is considered for the force term.

It is worth mentioning that the incompressible Navier-Stokes equations presented here are based on some assumptions (16, 17). These assumptions also apply to the coupled diffusion-flow model for simulating the gravity-driven flow in PMB. Firstly, it is assumed that PMB is a Newtonian fluid at the storage temperature (180 °C). According to some previous studies (18-22), this assumption can be true when the polymer content is not too high and the temperature is sufficiently high. It was reported that a PMB with 5% (by weight) waste polymer showed Newtonian behaviour from 140 °C upwards in the range of the tested shear rates. Thus, it is believed that this first assumption is reasonable for common paving PMBs. In addition, it is also assumed by the equations that the gravity-driven flow in PMB at the storage temperature is a laminar flow. Because the PMB is at rest in the beginning of the modelled process and its viscosity is relatively high, this second assumption is also believed to be true for PMB in this case.

As a two-phase flow is introduced into the model, the governing equations become coupled with each other. With a velocity vector involved, Equation 1 can be rewritten into the complete form of the Cahn-Hilliard equation (23-27) as

$$\frac{\partial \phi}{\partial t} + \nabla \cdot \mathbf{u} \phi = \nabla \cdot M(\phi) \nabla \frac{\delta F}{\delta \phi}. \quad (7)$$

In Equation 6, the density ρ and dynamic viscosity μ are dependent on the local composition of the phase as well as the properties of the individual components (polymer and bitumen). Under the incompressible condition, a linear dependency is postulated for the density in this paper, such that

$$\rho(\phi) = \rho_p \phi + \rho_b (1 - \phi), \quad (8)$$

where ρ_p is the density of the polymer modifier; and ρ_b is the density of the bitumen. The empirical Kendall-Monroe equation (28, 29) is employed to estimate the dynamic viscosity of the phase, i.e.

$$\sqrt[3]{\mu(\phi)} = \sqrt[3]{\mu_p} \phi + \sqrt[3]{\mu_b} (1 - \phi), \quad (9)$$

where μ_p is the dynamic viscosity of the polymer modifier; and μ_b is the dynamic viscosity of the bitumen. As for the force term $\mathbf{F}$, the following equation is used to represent the gravity, i.e.

$$\mathbf{F}(\phi) = \rho(\phi) \mathbf{g}, \quad (10)$$

where $\mathbf{g}$ is the acceleration of gravity (vector).

NUMERICAL SIMULATION RESULTS AND DISCUSSION

Simulation Environment and Parameters

The coupled diffusion-flow model described in the previous section has been implemented in the finite element software COMSOL Multiphysics. The numerical simulations are performed on a rectangular domain of 1.2 mm × 2.7 mm meshed with triangular elements.

This domain is in the vertical plane and basically three times the size of the microscopic images (magnification 100 $\times$) obtained in a previous experimental study by the authors (13). The complete geometry and mesh are shown in Figure 1. The domain is equally divided into three parts (bottom, middle and top) for the data post-processing and analysis. Thus, each of these three parts can represent a microscopic image of 1.2 mm $\times$ 0.9 mm. Boundary conditions are set by having the velocity (both u and v) being zero on all the four sides of the rectangle and the pressure being zero on the top side. Initial values of ϕ are generated by a normally distributed random function with a mean value of 0.05 and a standard deviation of 0.005. This means that the polymer content in the simulated PMB is 5% by volume with certain variation. If considering the density difference between the polymer and bitumen, the polymer content by weight is around 4.6%. The PMB is at rest ($u = v = 0$) in the beginning of the simulated process.

In order to simulate the gravity-driven flow in PMB at 180 °C, the needed parameters include the mobility coefficients (M_p and M_b), gradient energy coefficient κ , segment numbers of the chains (N_p and N_b), interaction parameter χ , dilution parameter z , densities (ρ_p and ρ_b) and dynamic viscosities (μ_p and μ_b). For N_p and N_b , this paper assumes that the hypothetical chains for bitumen have the same length as the polymer chains. It should be mentioned that N_b is not a simply averaged approximation of all molecules in the bitumen. Rather, N_b combines the effects of molecular size, distribution and their contributions to the configurational entropy. The values of M_p , M_b , κ , $N\chi$ and z can be calibrated by the comparison between the experimental and numerical results, while the values of ρ_p , ρ_b , μ_p and μ_b can be obtained by experimental measurements or using the related handbooks.

By setting different values for the material property parameters, the simulation cases listed in Table 1 are numerically implemented in this paper for evaluating: (i) the capacity of the coupled diffusion-flow model to predict storage stability (and instability) of PMB, and (ii) the effects of bitumen density and dynamic viscosity on the gravity-driven flow and phase separation in PMB at 180 °C. The first part of the simulations (Cases 1-3) uses the values of the parameters M_p , M_b , κ , $N\chi$ and z given in (8). These values were obtained by calibrating the diffusion model to reproduce the experimental results of three different PMBs with the same styrene-butadiene-styrene (SBS) copolymer modifier. The values of ρ_p , ρ_b , μ_p and μ_b are assumed to be constant in Cases 1-3 and the used values are based on the material producer data documents, handbooks and reported data in the literature (30-37).

Moreover, the second part of the simulations (Cases 4-7) uses constant values (same as Case 1) for the diffusion model parameters (M_p , M_b , κ , $N\chi$ and z) and investigates the influences of the possible variations of the bitumen density ρ_b and dynamic viscosity μ_b . The used bitumen density and dynamic viscosity values, selected on the basis of the data from bitumen handbooks and the related literature (30, 31, 36, 37), are intended to represent the most common bitumen grades (not specific bitumen). All the cases are run to simulate the storage at 180 °C for 5 hours. This does not represent the storage time in a real tube or tank, but a time scale corresponding to the simulated domain size.

Storage Stability of PMB

The simulation results of Cases 1-3 are shown in Figure 2. It can be seen that Case 2 is a stable case and Cases 1 and 3 are unstable cases. These results agree well with the simulation

results reported in (8). Since Cases 1-3 in this paper use the same values for the diffusion model parameters as in (8), it is not unexpected that they give the same predictions on storage stability of the simulated PMBs. However, because the gravity-driven flow is introduced into the model in this paper, the simulation results in Figure 2 show the PMB phase separation due to the polymer-bitumen density difference.

Case 2 represents a compatible case, and consequently, no separation happens in the simulated PMB. Thus, there is no two-phase structure formed and no density difference within the PMB. As a consequence, the gravity does not drive a flow in Case 2. With poor polymer-bitumen compatibility, Cases 1 and 3 start to separate into two phases by diffusion. After the density difference between the two phases forms, the gravity starts to drive the flow of the two phases and accelerate the separation in the vertical direction. As the used values for the diffusion model parameters in Case 1-3 were obtained by reproducing the experimental results of three different PMBs, it is interesting to see the good correlation between Figure 2 and the storage stability tube test results of the three PMBs reported in (13).

Furthermore, the gravity-driven flow and phase separation can be analysed by measuring the polymer content changes in different parts of the domain during the whole simulated process. In this paper, the domain is equally divided into three parts (bottom, middle and top, as shown in Figure 1a). The average polymer contents (by volume) are calculated from the values of the phase-field variable in the three different parts and the results of Cases 1-3 are presented in Figure 3.

Figure 3 gives the average contents of the pure polymer (not the polymer-rich phase) in different parts of the domain. It is indicated that the polymer contents in all the three parts of Case 2 always remain 5% by volume (i.e. the initial value, 4.6% by weight) during the simulation, showing the stability of this case. As for Cases 1 and 3, the polymer contents decrease in the bottom parts and increase in the top parts. This reveals the upward flows of the polymer-rich phases in both cases as the simulations continue. After 140 min, the polymer content reaches a plateau in the bottom part of Case 3. This is because almost all the polymer-rich phase has flowed to the upper parts from the bottom part, as seen in Figure 2. There are some polymer content fluctuations in the middle parts of Cases 1 and 3. The reason for these fluctuations is that the middle parts of Cases 1 and 3 have both inflow and outflow of the polymer-rich phases. But since 140 min, there has been only the outflow (no inflow due to the plateau in the bottom) for the middle part of Case 3. Consequently, the polymer content in this part starts to decrease from 140 min.

It can also be seen in Figure 3 that Cases 1 and 3 show different gravity-driven flows and phase separation behaviours. The separation in Case 3 is faster than Case 1. This is because these two cases use different values for the diffusion model parameters, showing different bitumen mobility and leading to different composition of the equilibrium phases. The higher M_b value results in faster bitumen diffusion in Case 3. The bigger composition difference causes bigger density and dynamic viscosity differences between the two equilibrium phases of Case 3, which gives rise to a faster flow. Thus, Case 3 has separated more than Case 1 by the end of the simulated process.

Effect of Bitumen Density

Cases 4 and 5 are intended to investigate the effect of bitumen density variation, using different ρ_b values from Case 1. The simulation results show the same equilibrium phase

composition and a similar separation process as the Case 1 results in Figure 2. However, the different bitumen density values lead to different levels of separation in Cases 4 and 5, especially at the end of the simulated process. The simulation results of Cases 4 and 5 at 300 min are shown in Figure 4. It can be seen that the polymer-rich phase of Case 5 has flowed more than that of Case 4. The polymer content curves in different parts of the domain, as presented in Figure 5, give more explicit information on this. For both cases, the polymer contents decrease in the bottom parts and increase in the top parts. There are some polymer content fluctuations in the middle parts. But the bigger polymer-bitumen density difference causes a bigger density difference between the two equilibrium phases of Case 5, which results in a faster flow. Consequently, Case 5 has separated more than Case 4 by the end of the simulated process, although the difference between the two cases is limited.

Effect of Bitumen Dynamic Viscosity

Cases 6 and 7 use different μ_b values from Case 1 and are intended to investigate the effect of bitumen dynamic viscosity variation. The simulation results also show the same equilibrium phase composition and a similar separation process as the Case 1 results in Figure 2. However, the different bitumen dynamic viscosity values also lead to different levels of separation in Cases 6 and 7, especially at the end of the simulated process. The simulation results of Cases 6 and 7 at 300 min are shown in Figure 6. It can be seen that the polymer-rich phase of Case 6 has flowed more than that of Case 7. The investigated variation of the dynamic viscosity μ_b seems to have a more significant influence than the investigated variation of the density ρ_b in this paper. This observation might depend on the specific values of the model parameters. More explicit information is given by the polymer content curves in different parts of the domain, as presented in Figure 7. For both cases, the polymer contents decrease in the bottom parts and increase in the top parts. There are some polymer content fluctuations in the middle parts. Lower bitumen dynamic viscosity, however, gives rise to lower dynamic viscosities of the two equilibrium phases of Case 6, which causes a faster flow. As a consequence, Case 6 has separated more than Case 7 by the end of the simulated process.

CONCLUSIONS AND FUTURE PERSPECTIVES

Conclusions

With the aim of predicting PMB storage stability, this paper presents a coupled diffusion-flow model and simulates the gravity-driven flow in PMB at storage temperature. By phase-field method, the incompressible Navier-Stokes equations are coupled with a previously proposed diffusion model for PMB phase separation. The effects of bitumen density and dynamic viscosity on the gravity-driven flow and phase separation in PMB are evaluated at 180 °C with the simulation results. On the basis of the numerical simulation results arising from the above described model, the following conclusions can be drawn:

- (i) The coupled diffusion-flow model gives the same predictions on PMB storage stability (and instability) as the diffusion model, provided that the same values for the mobility coefficients M_p and M_b , gradient energy coefficient κ , segment number of the chains N , interaction parameter χ and dilution parameter z are used. But the coupled model provides more information on the PMB phase separation due to the polymer-bitumen density

difference. A good correlation has been seen between the simulation results and the previously reported results of PMB storage stability tube test.

(ii) The polymer content changes in the different parts of the simulation domain reveal the upward flows of the polymer-rich phases in the unstable cases as the simulations continue. There is no gravity-driven flow in the compatible case. The different gravity-driven phase separation behaviours of PMBs may result from the different composition of the equilibrium phases in the PMBs as well as the different densities and dynamic viscosities of the individual components (polymer and bitumen).

(iii) A bigger polymer-bitumen density difference and/or a lower bitumen dynamic viscosity cause a faster flow and separation in the PMB at storage temperature. The investigated variation of bitumen dynamic viscosity (0.05-0.1 Pa·s at 180 °C) has a more significant influence than the investigated variation of bitumen density (927-937 kg/m³ at 180 °C) in this paper, but this might depend on the specific values of the model parameters.

Future Perspectives

The investigation reported in this paper is a preliminary exploration towards the understanding of the coupled diffusion-flow process in PMB related to the storage stability. With the outcome from this paper, further experimental and numerical studies will be conducted. Research focus will be placed on: (i) the experimental and numerical visualization of the gravity-driven flow in PMB at storage temperature, (ii) the composition-dependency of PMB density, dynamic viscosity and mobility coefficient, (iii) the effect of thermal condition on the gravity-driven flow and PMB morphology, and (iv) the experimental validation of the model by comparing with the numerical results of the same dimension. The results of this research are expected to have positive effects on designing PMB binders to ensure their storage stability. In addition, this study may also assist in developing a new test method for determining PMB storage stability in a more efficient way than the conventional tube test.

ACKNOWLEDGEMENTS

This study was partially funded by Nordiskt Vägforum (NVF, the Nordic Road Association). The authors greatly appreciate the financial support. The first author gratefully acknowledges the scholarship from the China Scholarship Council.

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FIGURE 7 Polymer content (by volume) changes in the bottom, middle and top parts of the simulated PMBs, Cases 6 and 7.

TABLE 1 Material Property Parameters Used in the Simulation Cases (180 °C)

Cases	M_p [m ⁵ /(J·s)]	M_b [m ⁵ /(J·s)]	κ [J/m]	$N\chi$	z	ρ_p [kg/m ³]	ρ_b [kg/m ³]	μ_p [Pa·s]	μ_b [Pa·s]
1	6.00×10^{-18}	6.75×10^{-18}	4.50×10^{-5}	2.9	8.7	855	932	2000	0.075
2	6.00×10^{-18}	1.80×10^{-17}	4.50×10^{-5}	1.9	7.0	855	932	2000	0.075
3	6.00×10^{-18}	1.80×10^{-17}	4.50×10^{-5}	3.6	7.0	855	932	2000	0.075
4	6.00×10^{-18}	6.75×10^{-18}	4.50×10^{-5}	2.9	8.7	855	927	2000	0.075
5	6.00×10^{-18}	6.75×10^{-18}	4.50×10^{-5}	2.9	8.7	855	937	2000	0.075
6	6.00×10^{-18}	6.75×10^{-18}	4.50×10^{-5}	2.9	8.7	855	932	2000	0.05
7	6.00×10^{-18}	6.75×10^{-18}	4.50×10^{-5}	2.9	8.7	855	932	2000	0.1

FIGURE 1 The geometry (*a*) and mesh (*b*) used for the simulations.

FIGURE 2 Simulation results of Cases 1-3 (warmer colours for the polymer-rich phase and cooler colours for the bitumen-rich phase).

FIGURE 3 Polymer content (by volume) changes in the bottom, middle and top parts of the simulated PMBs, Cases 1-3.

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