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Postprint

This is the accepted version of a paper published in *Materials & design*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

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

Zhu, J., Lu, X., Balieu, R., Kringos, N. (2016)

Modelling and numerical simulation of phase separation in polymer modified bitumen by phase-field method.

Materials & design, 107: 322-332

<http://dx.doi.org/10.1016/j.matdes.2016.06.041>

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Modelling and numerical simulation of phase separation in polymer modified bitumen by phase-field method

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Abstract

In this paper, a phase-field model with viscoelastic effects is developed for polymer modified bitumen (PMB) with the aim to describe and predict the PMB storage stability and phase separation behaviour. The viscoelastic effects due to dynamic asymmetry between bitumen and polymer are represented in the model by introducing a composition-dependent mobility coefficient. A double-well potential for PMB system is proposed on the basis of the Flory-Huggins free energy of mixing, with some simplifying assumptions made to take into account the complex chemical composition of bitumen. The model has been implemented in a finite element software package for pseudo-binary PMBs and calibrated with experimental observations of three different PMBs. Parametric studies have been conducted. Simulation results indicate that all the investigated model parameters, including the mobility and gradient energy coefficients, interaction and dilution parameters, have specific effects on the phase separation process of an unstable PMB. In addition to the unstable cases, the model can also describe and predict stable PMBs. Moreover, the phase inversion phenomenon with increasing polymer content in PMBs is also well reproduced by the model. This model can be the foundation of an applicable numerical tool for prediction of PMB storage stability and phase separation behaviour.

Keywords: Polymer modified bitumen; Storage stability; Phase separation; Phase-field method

1. Introduction

As an important material for road construction and maintenance, polymer modified bitumen (PMB) and its storage stability have been studied for decades [1-8], but the problem of PMB storage instability has still not been resolved for all cases [9]. With an improper selection of raw materials or production process, the polymer may separate from the bitumen during the PMB storage and transport. Considering PMB as a pseudo-binary blend, the phase behaviour of PMB has a very close relationship with its storage stability [10]. In this regard, the separation of polymer from bitumen in an unstable PMB is essentially a phase separation process, i.e. the separation of polymer-rich phase from bitumen-rich phase [11]. Many previous studies [1-5, 12-15] have experimentally investigated the effects of bitumen and polymer properties and their compatibility on the PMB morphology and storage stability. However, these studies found it difficult to demonstrate the key parameters controlling the phase separation process.

The phase separation in an unstable PMB is a complex process controlled by many factors. Diffusion and flow may be the main mass transfer modes in this process. In some cases, dynamic asymmetry between the bitumen and polymer may influence the mass transfer processes [10]. Due to the polymer-bitumen density difference, the gravity affects the PMB phase separation in the vertical direction. The gravity effect might, however, not be the direct cause for the separation, but could accelerate the phase separation in the vertical direction [11]. In the case of crystalline or semicrystalline polymer modifier (e.g. polyethylene and polypropylene), the polymer crystallization process may become important. With the use of chemically reactive additives (e.g. sulphur), chemical reactions certainly affect the phase separation. Last but not least, thermal history, i.e. the temperature level and its changing rate during phase separation, has significant effects on almost every factor mentioned above.

To investigate such a complex process, using only an experimental approach has the difficulty of separately identifying the influences of one factor from the others, as all the mass transfers and possible effects occur at the same time and are related to each other. A numerical approach, though often investigating a simplified system, has the advantage of enabling the investigation of every involved factor

separately and this allows for conclusions towards possible controlling parameters. As the continuation of a previous experimental study by the authors [11], this paper is considering a two-dimensional model for storage stability prediction of common PMBs and aims to develop a numerical model that is able to describe and predict the PMB phase separation behaviour. After a brief introduction to the theoretical background related to the phase-field modelling in the next section, the proposed expression of free energy for PMB system is discussed. Following the model development, numerical simulation results are compared with the experimental results and analysed under various conditions (for both unstable and stable cases), in order to separately identify the influence of every involved model parameter. In addition, the developed model is used to reproduce the phase inversion phenomenon with increasing polymer content in PMBs.

2. Theoretical background

2.1. Phase-field method

Phase-field method is a powerful approach to simulating the microstructure evolution of a wide variety of materials, e.g. polymer blends and alloys [16]. By this method, the material microstructure is represented by the phase-field variables (conserved or nonconserved) that are continuous across the interfacial regions, called diffuse interfaces [17]. The evolution of material microstructure is thus described by the temporal and spatial evolution of these phase-field variables, while the evolution of the phase-field variables is governed by a set of partial differential equations. The driving force for microstructural evolution is the minimization of free energy. Various forms of free energy can be considered. As phase-field method is a phenomenological method, the specific material properties must thus be introduced into the model through some phenomenological parameters that are determined based on the results of experimental measurements and theoretical calculation [17].

In order to simulate the phase separation in a binary blend using the phase-field method, the phase-field variable is the local composition. This is a typical conserved phase-field variable. Its evolution is governed by the Cahn-Hilliard equation, i.e.

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

where ϕ is the local composition; t is time; M is the mobility coefficient; and F is the free energy of the system. Based on Equation 1, different phase-field models can be derived from the different expressions of free energy. Generally, the free energy F of a system consists of local free energy (its density as f_{loc}), gradient energy (its density as f_{gr}) and long-range free energy F_{lr} , such that

$$F = \int_V (f_{loc} + f_{gr}) dV + F_{lr}, \quad (2)$$

where V is the volume of the considered body. The local free energy is the local contribution to the free energy, while the gradient energy originates from the short-range interactions at and around the interfaces. The sum of local free energy and gradient energy can also be divided into bulk free energy and interfacial energy. The long-range free energy is the nonlocal contribution to the free energy from the long-term interactions and it can be in the form of elastic energy, electrostatic energy, magnetic energy and so forth [16]. The specific expression of the free energy for a system must be determined in the context of the specific application. In this paper, the specific context of the modelling is a common PMB at the storage temperature.

2.2. Viscoelastic phase separation

Phase separation of viscoelastic matter is a very important fundamental phenomenon and it has been intensively studied for many years in the context of polymer blends. As the assumption of dynamic symmetry (the same dynamics for the two components of a binary mixture) is hardly valid in various real viscoelastic matters, Tanaka [18-20] introduced the concept of dynamic asymmetry (one slow component and one fast component) and complemented the traditional models with a viscoelastic model for phase separation in binary mixtures of viscoelastic matter. In Tanaka's model, the dynamic asymmetry may physically originate from the large difference in molecular size or glass transition temperature between the two components. The large difference leads to a considerably longer characteristic relaxation time of the slow component and thus potentially generates internal stresses within the mixture during the phase separation. The coupling between the generated internal stresses and the diffusion process plays an important role in the viscoelastic phase separation model.

Furthermore, the mobility of phases is strongly dependent on the phase composition. When the two components have very different glass transition temperatures, the strong dependency of mobility on phase composition may have similar effects on the phase separation process as the stress-diffusion coupling [20].

3. Phase-field modelling for phase separation in PMB

As the continuation of a previous experimental study by the authors [11], this paper is considering a two-dimensional model for storage stability prediction of common PMBs. In this, a first simplification is made to not consider the effects of polymer-bitumen density differences, crystallization and possible chemical reactions. The importance of these on the actual phase separation process and thus the ability of the current model to capture the dominant process need to be further investigated in future research. Since the effects of flow were minimized in [11], in this paper a diffusion model with viscoelastic effects based on the Cahn-Hilliard equation (Equation 1) is further explored. Defining ϕ as the local fraction of polymer in the PMB, the viscoelastic effects due to the dynamic asymmetry between bitumen and polymer are represented in this paper by introducing an ϕ -dependent phase mobility coefficient $M(\phi)$. Under the incompressible condition, a linear dependency of the mobility coefficients of the polymer and bitumen, M_p and M_b respectively, is postulated such that

$$M(\phi) = M_p\phi + M_b(1 - \phi) . \quad (3)$$

Besides the dependency of the mobility coefficient on the local composition, the only variable that needs to be determined is the free energy of the PMB system.

The expression of the free energy for PMB system has to be based on the fact that bitumen is a complex mixture of various molecules. Bitumen composition and its molecular chemistry certainly have very strong influences on the free energy of PMB system. Since this paper is considering storage stability prediction of common road paving PMBs, the discussed temperature level is fixed and quite high, e.g. usually around 180 °C for styrene-butadiene-styrene (SBS) modified bitumen. At such a high temperature, there is actually no coherent microstructure formed in the PMB. Consequently, elastic energy (usually generated during solid-solid phase transformation) is not involved in this case [21, 22]. Neither are other forms of long-range free energy. In this regard, for PMB, Equation 2 can be rewritten such as

$$F = \int_V (f_{loc} + f_{gr}) dV . \quad (4)$$

The common expression of the gradient energy density f_{gr} [16, 17, 23-27], given by

$$f_{gr} = \frac{1}{2} \kappa |\nabla \phi|^2 , \quad (5)$$

is used in the model. In Equation 5, κ is the gradient energy coefficient.

Considering PMB as a pseudo-binary blend, the local free energy of the system includes the free energy of pure polymer and bitumen as well as the free energy change due to mixing the two components, i.e.

$$f_{loc} = f_0 + \Delta f_m , \quad (6)$$

where f_0 is the free energy density of pure components (sum of polymer and bitumen) and Δf_m is the free energy density change due to mixing. For a given blend, the free energy of the pure components keeps constant at a fixed temperature. The free energy of mixing can be represented by a double-well potential (Figure 1 B). The minimization of free energy determines the composition of equilibrium phases and thus the location of binodal points at the fixed temperature. A double tangent can be constructed to the free energy curve at the binodal points, which shows the homogenization of chemical potential throughout the whole equilibrium system. The plot of all binodal points at different temperatures gives the binodal curve on phase diagram of the blend (Figure 1). Furthermore, another curve on the phase diagram, the spinodal curve, can be constructed by plotting all the inflection points (where the curvature equals to 0) of the free energy curves at different temperatures. In this regard, a positive curvature on the free energy curve usually represents the one-phase or metastable state, while a negative curvature means the unstable state.

Some previous investigations [14, 28] have observed that SBS modified bitumen separates upon cooling and shows an upper critical solution temperature (UCST) on the phase diagram. In this case, when the temperature is high enough (e.g. T_1 in Figure 1), the chemical potential can be homogeneous throughout the whole system at any composition. With a fixed composition (e.g. ϕ_0 in Figure 1), as the temperature decreases, the blend may go through a metastable state (e.g. T_2 in Figure 1) and finally reach an unstable state (e.g. T_3 in Figure 1). If ϕ is defined as the polymer fraction in PMB, at fixed temperature (e.g. T_2 and T_3 in Figure 1), the blend may also lie in different state regimes on the phase diagram as the ϕ value increases. However, it is worth mentioning that a very high ϕ value (i.e. a very high polymer fraction in PMB) usually cannot result in a one-phase PMB structure. This is due to the complex chemical composition of bitumen. Additionally, very high polymer content is not a common practice for road paving in reality. So the high- ϕ -value area on a PMB phase diagram (at least the shaded area in Figure 1) is not of practical concern regarding the potential application on PMB.

Figure 1. Phase diagram (A) and free energy curves (B). ϕ_0 represents the initial composition; ϕ_2' and ϕ_2'' represent the equilibrium phase composition at temperature T_2 ; and ϕ_3' and ϕ_3'' represent the equilibrium phase composition at temperature T_3 . The black dots on free energy curves represent the inflection points.

In order to obtain the expression of the free energy, a double-well potential for PMB system can be determined on the basis of the Flory-Huggins free energy of mixing [18-20, 23-26]. The Flory-Huggins theory was originally proposed for polymer solutions by taking into account their differences with an ideal solution, i.e. the nature of long polymer chains and the asymmetric interaction between polymer and the solvent. It uses a lattice to represent the solution, as illustrated in Figure 2. Each cell in the lattice has the same volume. It is assumed that each solvent molecule occupies one cell in the lattice and each polymer chain occupies a set of neighbouring cells, seen in Figure 2 (A). By statistical thermodynamics calculation, the free energy density of mixing for polymer solutions can be expressed by

$$\Delta f_m = RT[c_1 \ln(\phi_1) + c_2 \ln(\phi_2) + c_1 \phi_2 \chi], \quad (7)$$

where R is the universal gas constant; T is the temperature; c_1 is the molar concentration of the solvent; ϕ_1 is the local volume fraction of the solvent; c_2 is the molar concentration of the polymer; ϕ_2 is the local volume fraction of the polymer; and χ is the interaction parameter between the solvent and polymer. The first two terms in the square brackets on the right-hand side of Equation 7 are related to the entropy of mixing, while the last term is related to the heat of mixing. The interaction parameter χ characterizes the energy change due to mixing of one solvent molecule and thus shows the degree of interaction between the solvent and polymer. χ is a parameter dependent on temperature and the local composition.

As for polymer blends, the two different kinds of polymer chains respectively occupy some neighbouring cells in the lattice, shown in Figure 2 (B). In this case, the statistical thermodynamics calculation gives the free energy density of mixing for polymer blends as

$$\Delta f_m = RT \left[\frac{\phi_1}{V_1} \ln(\phi_1) + \frac{\phi_2}{V_2} \ln(\phi_2) + \frac{\phi_1 \phi_2 \chi}{V_c} \right], \quad (8)$$

where ϕ_1 and ϕ_2 are the local volume fractions of the two polymers; V_1 and V_2 are the molar volumes of the two polymers; V_c is the molar volume of the cells; and χ is the interaction parameter between the two polymers. Since Equation 8 contains a parameter for the hypothetical lattice (V_c), the discussed volume is usually set as the molar volume of the cells. Then, Equation 8 can be rewritten without affecting the minimization of the free energy such that

$$\Delta f_m = RT \left[\frac{\phi_1}{N_1} \ln(\phi_1) + \frac{\phi_2}{N_2} \ln(\phi_2) + \phi_1 \phi_2 \chi \right] \quad (9)$$

where N_1 and N_2 are the segment numbers of (i.e. cell numbers occupied by) the two polymer chains. The parameters N_1 and N_2 , showing the size of the polymer chains, are not necessarily equal to but proportional to the degree of polymerization and molecular weight of the polymers.

Figure 2. Flory-Huggins lattices for polymer solutions (A) and polymer blends (B). The blue colour represents the solvent; and the red and green colours represent different polymers.

The Flory-Huggins theory is an approximation theory for which some simplifying assumptions are made. In order to determine the expression of the free energy for PMB, certain simplifications must be made for the PMB system accordingly. The common polymer modifiers used in PMB are industrially synthesized products where branching usually happens during the synthesis. In order to hypothesize a lattice for PMB, all the polymer chains are simplified into straight chains. In the case of copolymer, different structural units exist in the polymer chains. A hypothetical lattice for SBS modified bitumen is shown in Figure 3. However, further approximation based on molar volume (or molecular weight) of the SBS copolymers still needs to be made to have hypothetical chains with single segment size like Figure 2.

Bitumen, the other component in PMB, is a complex mixture consisting of a continuum of relatively large hydrocarbons. The hydrocarbons are different in size, polarity and aromaticity. The exact range of molecular size varies from case to case, depending on the production process and crude oil source. But it is estimated that the size of hydrocarbons in bitumen may range from 20 up to 110 carbons [29]. In

order to hypothesize a lattice for PMB, the molecules in bitumen are simplified into molecules of different sizes, as indicated in Figure 3. It is worth mentioning that, for a better visibility, Figure 3 does not show the actual molar volume (or molecular weight) ratio between bitumen molecules and SBS copolymer chains. From Figure 3, it can be seen that PMB is neither a typical polymer solution case nor a typical polymer blend case. Furthermore, because of the property diversity, it is not reasonable to simply approximate the bitumen molecules into molecules of the average size. However, due to the size diversity of bitumen molecules, configurational entropy can arise from the variety of ways of arranging the bitumen molecules in the lattice, which has similar effects as the arrangement of the polymer chains. Thus, it is believed that the bitumen molecules in Figure 3 can be further approximated into hypothetical chains with single segment size like Figure 2. In this regard, the hypothetical chains will have an equivalent molar volume (and equivalent molecular weight) that is different with the actual parameter of the bitumen.

Figure 3. Hypothetical lattice for styrene-butadiene-styrene (SBS) modified bitumen. Blue=bitumen; red=polystyrene blocks in SBS; and green=polybutadiene blocks.

Additionally, the Flory-Huggins theory does not properly describe the swelling of polymer in PMB. This theory gives good approximations on the fluxes of the two phases only when the polymer content of the PMB is sufficiently high. Due to the complex composition of bitumen, in a given PMB, the bitumen molecules might show a continuum of χ values with the polymer. Some of the molecules may be very interactive with the polymer, while some others may be not interactive at all. The polymer swells by absorbing the interactive molecules of bitumen, but it is just very few polymer chains that go into the bitumen-rich phase. The extent of polymer swelling thus depends on the amount of interactive molecules in the bitumen. In this regard, for describing the interaction between polymer and the hypothetical chain of bitumen, the amount of interactive molecules in bitumen becomes as important as the degree of interaction between polymer and these interactive molecules.

Consequently, a new parameter, named *dilution parameter* in this paper, is introduced into the model as a simplification for taking the influence of the interactive molecules amount into account. The meaning of this parameter can be interpreted by a hypothetical dilution process. Some previous

investigations [1, 30] have observed that the swelling ratio of the polymer in PMB decreases when the polymer content increases, lightly or sharply depending on the material properties and discussed range of polymer content. Within the practical range of polymer content in PMB, the swelling ratio is relatively high and can be up to nine (by volume in the three-dimensional case and by area in the two-dimensional case) [31]. The assumption is to take a representative part of the bitumen like one column of cells in Figure 4, which has the same composition as the original bitumen, to achieve the high-polymer-content interaction between polymer and the hypothetical chain of bitumen assumed by the Flory-Huggins theory with respect to a representative χ value. At this moment, the blend represents the case with sufficiently high polymer content. After this, all the other parts of the bitumen (i.e. all the other cells in Figure 4) are supposed to dilute the blend as a simplification for polymer swelling. As the relative amount of interactive molecules in bitumen decides how much the representative part is, the dilution parameter can thus reflect the influence of the interactive molecules amount in bitumen. In this sense, it is a parameter which depends on the temperature and the local composition.

Figure 4. The dilution assumption for simplifying the modelled PMB phase separation process. Each cell in the figure may represent different amounts of molecules in the bitumen.

Based on the above discussion, defining ϕ as the local volume fraction of the polymer in PMB and under the incompressible condition, the proposed free energy density of mixing for PMB can be expressed by

$$\Delta f_m = RT \left[\frac{z\phi}{N_p} \ln(z\phi) + \frac{1-z\phi}{N_b} \ln(1-z\phi) + z\phi(1-z\phi)\chi \right], \quad (10)$$

where N_p is the segment number of the polymer chain; N_b is the segment number of the hypothetical chain for bitumen; and z is the dilution parameter. In the equation, N_p and N_b characterize the molecular size (and its distribution for bitumen) of the polymer and bitumen; χ characterizes the degree of interaction between polymer and bitumen; and z characterizes the relative amount of interactive molecules in the bitumen. Although the molecular size and distribution of bitumen varies from case to case, it is believed that influence of the variety on the configurational entropy is not significant. N_b is thus considered as a constant parameter for different bitumen binders. In this regard, for given polymer modifier and temperature, the values of χ and z can define the free energy of mixing for PMB and consequently the equilibrium phase composition. It is worth mentioning that the dilution parameter z actually includes the effects of polymer content in PMB.

4. Numerical simulation results and discussion

4.1. Simulation environment and parameters

The model described in the previous section has been implemented in the finite element software COMSOL Multiphysics for pseudo-binary PMBs. The numerical simulations are performed on a rectangular domain of 1.2 mm×0.9 mm meshed with triangular elements. This domain is basically the same size as the microscopic images obtained in the previous study by the authors [11]. The complete mesh consists of 18708 domain elements and 350 boundary elements, as shown in Figure 5. Boundary conditions are set by having a contact angle of 90° on the four sides of the rectangle. Initial values are generated by a normally distributed random function with a mean value of 0.05 and a standard deviation of 0.005, as presented in Figure 6. This means that the polymer content in the simulated PMB is 5% by weight with certain variation, if neglecting the density difference between the polymer and bitumen. It can be seen from Figure 6 that the local polymer volume fraction in the PMB can range from 3.11% up to 7.13%, which is believed to represent the actual initial condition of a real PMB. Within the limits, the specific range may vary from case to case depending on the parameters.

Figure 5. The geometry (in mm) and finite element mesh used for the simulations.

Figure 6. The normally distributed random function with a mean value of 0.05 and a standard deviation of 0.005.

For the model implementation, 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 and dilution parameter z are needed. Theoretically, the mobility coefficient $M(\phi)$ is a variable related to the interdiffusion (or chemical diffusion) coefficient $D(\phi)$ between the two components [17] given by

$$M(\phi) = \frac{V_m D(\phi)}{\partial^2 f_m / \partial \phi^2}, \quad (11)$$

where V_m is the molar volume of the phase and f_m is the molar free energy of the system. $D(\phi)$ is a variable related to the self-diffusion (or tracer diffusion) coefficients of the individual components. If sufficient information is available, $M(\phi)$ can be determined by: 1) experimental measurements of the diffusion coefficients or 2) theoretical calculation with the atomic mobility coefficients of the constituting elements. As diffusion coefficient measurements are still not performed very commonly for PMBs and there is still a lack of related thermodynamic and chemical information, this paper uses the values of M_p and M_b to determine $M(\phi)$ (Equation 3), instead of a direct determination. The gradient energy coefficient κ is a positive parameter related to the interfacial tension and thickness between the phases (if more than one phase) [17]. Considering the length scale of the interfaces, κ can only be determined by interactive procedures between computational models and available experimental characterization techniques [32], which have not been widely reported or studied for PMBs. Due to the lack of available data for PMBs, the used ranges of M_p , M_b and κ in this paper are obtained by preliminary estimation based on the reported values for general models and other materials like polymer blends and alloys [25, 33-35].

For all the simulations in this paper, the universal gas constant R equals to 8.314 J/(mol·K) and the temperature is constant at 180 °C (453.15 K). For N_p and N_b , it is assumed that the hypothetical chains for bitumen have the same length as the polymer chains. This means that N_p and N_b have the same value in this paper. In this regard, Equation 10 can be reduced into a simple mathematical form by setting $N_p = N_b = 1$ without affecting the minimization of the free energy. Thus, the interaction parameter χ also accordingly scales up into the widely reported theoretical range where $\chi \leq 2.0$ results in a single well and $\chi > 2.0$ leads to a double well [23, 24, 26, 32]. As for the dilution parameter z , the values can be preliminarily estimated based on the reported swelling ratio values of polymer in PMB. According to the measurement results by [1, 30, 31], it is believed that z may range from 5.0 to 9.0 in most cases within the practical range of polymer content in PMB.

4.2. Experimental characterization and numerical reproduction

With the theoretical ranges of the model parameters, the specific values can then be calibrated by the comparison between the experimental and numerical results. Experimentally, the phase separation behaviour of three different PMBs (numbered I, II and III) with the same SBS copolymer modifier (5% by weight of the blend) was observed with a microscope. The experimental procedure represented the same condition as the numerical simulation: the thin film method [14] was used for sampling and isothermal annealing conditioning was conducted at 180 °C. Two light sources were used, i.e. ultraviolet (UV) and white light. The fluorescence images with UV (presented in [11]) have confirmed that the images with white light, shown in Figure 7, display the binary phase microstructures of the PMBs. It can be seen from Figure 7 that PMB I and PMB III separated into two phases: the lighter SBS-rich phase and the darker bitumen-rich phase. PMB II remained homogeneous at this scale. For more details on the experimental procedure, please refer to [11]. The model parameters calibrated to reproduce these experiments are shown in Table 1. The simulation results of the three cases are also shown in Figure 7, following the microscopy images. It is indicated that the phase separation behaviour of the PMBs are well reproduced by the model, including stable and unstable cases. The unstable Case 1 and Case 3 show different patterns and evolution, similar as the experimental results for PMB I and PMB III.

Table 1. Calibrated parameter values for Cases 1, 2 and 3, representing PMBs I, II and III.

Cases	M_p [m ⁵ /(J·s)]	M_b [m ⁵ /(J·s)]	κ [J/m]	χ	z
1	2.25×10^{-18}	6.75×10^{-18}	4.50×10^{-5}	2.9	8.7
2	6.00×10^{-18}	1.80×10^{-17}	4.50×10^{-5}	1.9	7.0
3	6.00×10^{-18}	1.80×10^{-17}	4.50×10^{-5}	3.6	7.0

Figure 7. Microscopy observation and numerical simulation results of the three different PMBs.

4.3. Parametric studies

In order to show and understand the influence of each involved parameter, parametric studies are conducted by having six additional cases with the listed values in Table 2. Together with the cases in Table 1, all the studied cases are intended to represent various conditions: Cases 1, 4 and 5 for studying the effects of the mobility and gradient energy coefficients, Cases 3, 4, 6 and 7 for studying the interaction and dilution parameters, and Cases 2, 8 and 9 for stable systems. The independency between M_p and M_b is hereby not investigated in the parametric study cases. This means that M_p and M_b always varies with the same rate between the cases in this paper, instead of individual rates.

Table 2. Additional parametric study cases.

Cases	M_p [$\text{m}^5/(\text{J}\cdot\text{s})$]	M_b [$\text{m}^5/(\text{J}\cdot\text{s})$]	κ [J/m]	χ	z
4	6.00×10^{-18}	1.80×10^{-17}	4.50×10^{-5}	2.9	8.7
5	6.00×10^{-18}	1.80×10^{-17}	9.00×10^{-6}	2.9	8.7
6	6.00×10^{-18}	1.80×10^{-17}	4.50×10^{-5}	3.6	8.7
7	6.00×10^{-18}	1.80×10^{-17}	4.50×10^{-5}	2.9	7.0
8	6.00×10^{-18}	1.80×10^{-17}	4.50×10^{-5}	2.1	9.0
9	2.40×10^{-21}	7.20×10^{-21}	9.00×10^{-7}	2.9	8.7

The parametric study results are shown in Figure 8. The effect of the mobility coefficients (M_p and M_b) can be seen by comparing Case 1 and Case 4. Because Case 1 has lower mobility coefficients than Case 4, the phase separation process occurs more slowly in Case 1. It is noticed that the result at 1800 s in Case 1 is quite similar as the result at 600 s in Case 4. Thus, Case 1 allows us to look into the early stage of a fast separation. In Case 1, the polymer-rich phase (warmer colours) is continuous at 300 s. As the separation process continues, the polymer-rich phase becomes dispersed and coarsens. Since it is only very slight dynamic asymmetry between bitumen and polymer that is introduced into the model, this phase inversion phenomenon may be just partially due to the ϕ -dependent mobility coefficient. However, more research still needs to be done for understanding and incorporating strong viscoelastic effects in the model. The inversion process also happens in Case 4 before 300 s. Furthermore, the implication of the gradient energy coefficient κ can be seen by comparing Case 4 and Case 5. With a lower gradient energy coefficient, Case 5 displays a finer structure and sharper interfaces than Case 4. Controlled by the interaction parameter χ and the dilution parameter z , the equilibrium phase composition (polymer volume fraction) of Cases 1, 4 and 5 keeps the same, i.e. 10.7% for polymer-rich phase and around 0.9% for bitumen-rich phase. This simulation result agrees well with the experimental measurement results by other researchers [15].

The influences of the interaction parameter χ and dilution parameter z can be seen by comparing Cases 3, 4, 6 and 7. As χ reflects the energy change due to mixing and z characterizes the relative amount of interactive molecules in the bitumen, a lower χ value (i.e. lower energy change and easier interaction) indicates a higher degree of interaction between the polymer and bitumen and a higher z value means the relative amount of interactive molecules in the bitumen is higher. Thus, Cases 3, 4, 6 and 7 can represent various conditions of polymer-bitumen interaction. It can be seen that the four cases all have different values of polymer volume fraction as the equilibrium phase composition. A lower χ value leads to a lower polymer fraction in the polymer-rich phase and higher polymer fraction in the bitumen-rich phase, whereas a higher z value results in a lower polymer fraction in the polymer-rich phase. This reflects the reality in PMBs. When the degree of polymer-bitumen interaction is higher, the PMB tends to form a more homogeneous blend. If the relative amount of interactive molecules in the bitumen is higher, more bitumen molecules can interact with the polymer chains and thus reduce the polymer fraction in the polymer-rich phase. Since the local composition dependency of χ has not been introduced into the model in this paper, the effect of z on equilibrium phase composition is still not properly shown in the bitumen-rich phase in the studied cases.

In addition, the numerical simulation results also reveal that Case 7, with lower χ values than Case 3, takes longer time to reach the equilibrium state. This can be interpreted as an indication that with an increasing degree of polymer-bitumen interaction the separation process becomes more difficult. Last but not least, it is obvious from Figure 8 that the cases with higher z values (Case 4 and Case 6) have higher area fractions of the polymer-rich phase in the results. This represents what actually happens in real PMBs. When the relative amount of interactive molecules in the bitumen is higher, more bitumen molecules can interact with the polymer chains and thus form more areas of polymer-rich phase in the PMB. If defining the polymer-rich phase as the area where the local volume fraction of the polymer is higher than the mean of the initial values (5%), the polymer swelling ratio can be defined as the ratio between the area fraction of the polymer-rich phase and the mean of the initial values. By post-processing the simulation results, the swelling ratio values

Figure 8. Numerical simulation results of the additional parametric study cases.

during the whole phase separation process can be obtained, as shown in Figure 9 for the unstable cases. It can be seen in Figure 9 that all the cases start with the swelling ratio value of 10, due to the normal distribution of the initial values. The cases end up with two groups of values as the polymer swelling ratio, which is controlled by the two z values. During the phase separation, the changes of the swelling ratio values reflect the process of reaching the equilibrium state from the initial state. Among Cases 1, 4 and 5, Case 5 takes the shortest time to get to the equilibrium swelling ratio value. A higher gradient energy coefficient (Case 4) and lower mobility coefficients (Case 1) can make the separation process longer. With higher χ values, Case 6 takes shorter time than Case 4 and Case 3 takes shorter time than Case 7 to reach the equilibrium swelling ratio values. These conclusions confirm what have been observed in Figures 7 and 8.

Figure 9. Polymer swelling ratio during phase separation.

Besides the unstable cases, three stable cases (Cases 2, 8 and 9, representing different possibilities for stable PMBs) are also included in the parametric studies. Cases 2 and 8 are the thermodynamically stable cases. Case 2 uses a χ value less than 2.0, which means the degree of polymer-bitumen interaction is high enough to have a single well for the free energy of mixing. Thus, an absolutely homogeneous structure is formed in the PMB. Case 8 uses a very high z value and a relatively low χ value (greater than but close to 2.0). This means the relative amount of interactive molecules in the bitumen is very high and the degree of polymer-bitumen interaction is relatively high but not high enough to have a single well for the free energy of mixing. So the simulated PMB can lie in the one-phase regime on the phase diagram and form an absolutely homogeneous structure. Case 9 represents the thermodynamically unstable case with sufficiently low mobility and gradient energy coefficients. In this case, a phase separation still happens in a very small scale. However, because of the extremely fine structure of the pseudo-binary blend, microscopy or other available experimental techniques may not be able to capture the structure and still recognize it as a stable case for the PMB.

4.4. Phase inversion with increasing polymer content

Some previous studies [31, 36-39] reported the phase inversion phenomenon with increasing polymer content in PMBs. It is a fundamental phenomenon for some PMBs. Despite the same name, it is a different phenomenon with the previously mentioned phase inversion which is one main feature of viscoelastic phase separation. The model presented in this paper has been used to reproduce the phase inversion with increasing polymer content. Six cases are implemented with the mean of initial values at 0.03, 0.04, 0.05, 0.06, 0.07 and 0.08. The standard deviation of initial values is the same as the previous cases. This means that the polymer contents in the simulated PMBs are from 3% up to 8% by weight of the PMB blends, if neglecting the density difference between the polymer and bitumen. The parameters of the Case 1 are used for the 0.05 case. Since the dilution parameter z characterizes the relative amount of interactive molecules in the bitumen, the z value is actually affected by the polymer content in PMB. Thus, different z values should be used in the simulation for varying polymer contents. According to the reported decreasing trend of polymer swelling ratio with increasing polymer content in PMBs [1, 30], the used z values are 8.9, 8.8, 8.7, 8.6, 8.5 and 8.4 respectively. The simulation results at 3600 s of the six cases are shown in Figure 10. It can be seen that the phase inversion phenomenon with increasing polymer content in PMBs is well reproduced by the model: from bitumen being the dominant continuous phase to polymer becoming the dominant continuous phase.

Figure 10. Simulation results on phase inversion with increasing polymer content.

4.5. Limitations

As mentioned in the previous section, phase-field method is a phenomenological method. Almost all the model parameters, as described in this paper, are phenomenological parameters that need to be determined based on the results of experimental measurements and theoretical calculation. Due to the lack of available data for PMBs today, precise determination of material parameters still remains an issue. It may be resolved as the release of more data in the future and the finding of potential empirical correlations between some easily-measurable parameters and the model parameters. In addition, because of the complex chemical composition of bitumen, some assumptions and simplifications are made for the model development, which also causes some limitations of the model. One example has been mentioned in the previous section: the effect of z on equilibrium phase composition is not properly shown in the bitumen-rich phase in the studied cases, although this may be fixed by introducing the local composition dependency of χ into the model. Depending on the parameters, another example of limitation is the model may give wrong results when comparing two stable cases with very high z values and relatively low χ values (similar cases like Case 8). All these limitations will be taken into consideration for the future development of the model.

5. Conclusions

Storage stability is the primary requirement for all PMBs, so understanding the stability-related phase behaviour of PMB is of great importance for ensuring the storage stability. The phase separation process in an unstable PMB is affected by many factors, e.g. the bitumen composition, polymer chemistry and content, density and viscosity of the bitumen and polymer. Aiming to describe and predict the storage stability and phase separation behaviour of common PMBs, a phase-field model with viscoelastic effects is developed based on the Cahn-Hilliard equation in this paper. The viscoelastic effects due to dynamic asymmetry between the bitumen and polymer are represented in the model by introducing an ϕ -dependent mobility coefficient. Regarding the expression of the free energy, a double-well potential for PMB system is proposed on the basis of the Flory-Huggins free energy of mixing, with some assumptions made according to the complex chemical composition of bitumen. The proposed model is able to reproduce the phase separation behaviour of the three PMBs observed experimentally. On the basis of the above described model and the numerical simulation results, the following conclusions can be drawn:

- (1) Parametric studies indicate that lower mobility coefficients of polymer and bitumen make the PMB phase separation process slower, while a lower gradient energy coefficient between the polymer and bitumen results in a faster separation as well as a finer PMB structure and sharper interfaces. The phase inversion phenomenon is observed in a low-mobility case, which is believed to be partially due to the ϕ -dependent mobility coefficient. More research, however, still needs to be done for understanding and incorporating strong viscoelastic effects in the model.
- (2) A lower interaction parameter value between the polymer and bitumen leads to a lower polymer fraction in the polymer-rich phase and higher polymer fraction in the bitumen-rich phase, whereas a higher dilution parameter value of the bitumen causes a lower polymer fraction in the polymer-rich phase. In addition, a lower interaction parameter value also slows down the separation process, while a higher dilution parameter value makes the polymer swell more.
- (3) Besides the unstable cases, the presented model in this paper can also describe and predict stable PMB cases: including the thermodynamically stable cases with single or double wells for the free energy of mixing and thermodynamically unstable case with sufficiently low mobility and gradient energy coefficients.
- (4) The phase inversion phenomenon with increasing polymer content in PMBs is well reproduced by the presented model in this paper: from bitumen being the dominant continuous phase to polymer becoming the dominant continuous phase.
- (5) In order to improve the model, more future work still can be done, e.g. introducing the dependency of some model parameters on local composition. Furthermore, the determination of material parameters can also be further studied, e.g. the correlation between the solubility parameters of the materials and the interaction and dilution parameters of the model.

Acknowledgements

The authors thank Petri Uhlbäck from Nynas AB for his assistance on the experiments. The first author gratefully acknowledges the scholarship from the China Scholarship Council.

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