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.

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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

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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.

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

where $\varnothing$ is the local composition; t is time; M is the mobility coefficient; and F is the free energy of the system. Based on Eq. (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

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

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 (Eq. (1)) is further explored. Defining $\varnothing$ 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 $\varnothing$-dependent phase mobility coefficient $M(\varnothing)$. 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

$$M(\varnothing) = M_p \varnothing + M_b (1 - \varnothing). \tag{3}$$

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, Eq. (2) can be rewritten such as

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

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

$$f_{gr} = \frac{1}{2} \kappa |\nabla \varnothing|^2, \tag{5}$$

is used in the model. In Eq. (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.

$$f_{loc} = f_0 + \Delta f_m, \tag{6}$$

where f_0 is the free energy density of pure components (sum of polymer