Characterization and Modelling of Phase Separation in Polymer Modified Bitumen

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ABSTRACT

In this study, the phase separation behaviour of polymer modified bitumen (PMB) is characterized at the storage temperature by the fluorescence microscopy. A phase-field model for predicting PMB storage stability is described. The model is expected to have a positive effect on designing PMB binders to ensure their storage stability.

INTRODUCTION

Polymer modified bitumen (PMB) is an important material for road construction and maintenance. Some popular polymer modifiers for bitumen include polyethylene (PE), polypropylene (PP), ethylene-vinyl acetate (EVA) and styrene-butadiene-styrene (SBS). These polymers were reported to improve some properties of bitumen. However, they have also caused various problems[1].

One of the identified common problems for PMB was the storage instability of the final PMB products, i.e. the separation of polymer from bitumen during storage and transport[2]. Since the storage stability is the primary requirement for all PMBs, understanding the stability-related phase behaviour beforehand of PMB is thus of great importance.

Starting from fluorescence microscopy investigation, a constitutive model is developed in this study to simulate and understand the PMB phase behaviour and phase separation phenomena. Research focus is placed on PMB structure, equilibrium thermodynamics and phase separation dynamics. Having such a model available is expected to have a positive effect on designing PMB binders to ensure their storage and transport stability and enhance their performance. The use of these kinds of materials can have a significant impact on the sustainability of roads.

MICROSCOPY OBSERVATION

The phase separation processes in four different PMBs with the same SBS copolymer modifier (5% by weight of the blend) were captured by fluorescence microscope. The thin film method[3] was used for the sampling. After preparation, the samples were conditioned by isothermal annealing at 180 °C for 60 min. The fluorescence microscopy images of the PMBs after the conditioning are shown in Fig. 1.

It can be seen from Fig. 1 that PMB1 and PMB4 separated into two phases: the lighter SBS-rich phase and the darker bitumen-rich phase. PMB2 and PMB3 remained homogeneous at this scale. In order to understand the reasons for the morphological differences between the PMBs, a phase-field model is developed to simulate the PMB phase separation behaviour.

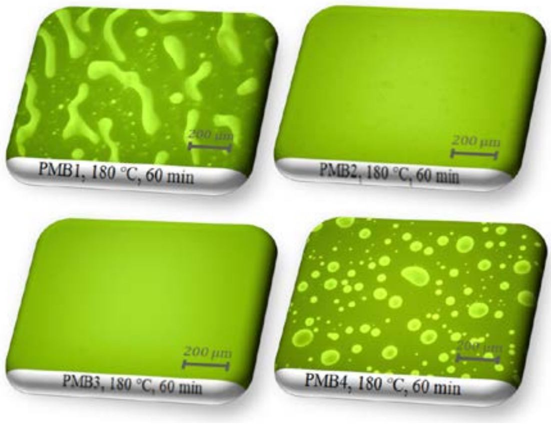

Figure 1. Fluorescence microscopy images of the PMBs after isothermal annealing conditioning at 180 °C for 60 min.

PHASE-FIELD MODELLING

Phase-field modelling is a powerful method for the simulation of microstructure evolution in various materials. For modelling the phase separation in PMB, the phase-field variable is the local volume fraction of the polymer modifier, which is a typical conserved phase-field variable[4]. Its evolution is governed by the Cahn-Hilliard equation, i.e.

$$\frac{\partial \emptyset}{\partial t} = \boldsymbol{\nabla} \cdot M(\emptyset)\boldsymbol{\nabla}\frac{\delta F}{\delta \emptyset} \qquad (1)$$

where $\emptyset$ is the local volume fraction of the polymer in PMB; t is the time; $M(\emptyset)$ is the mobility coefficient; and F is the free energy of the PMB.

The expression of the free energy F in Eq. 1 for PMB has to be based on the fact that bitumen is a complex mixture of various molecules. The specific context of the modelling in this study is a PMB at the storage temperature (180 °C). In this regard, the free energy of PMB consists of local free energy and gradient energy, such that

$$F = \int_V \left(f_{loc} + \frac{1}{2}\kappa|\boldsymbol{\nabla}\emptyset|^2\right) dV \qquad (2)$$

where V is the volume of the considered body; f_{loc} is the local free energy density; and κ is the gradient energy coefficient.

In Eq. 2, the local free energy density f_{loc} for PMB can be approximated on the basis of the Flory-Huggins free energy of mixing. By comparing the numerical simulations with the experimental results, the model parameters can be estimated and the phase separation in PMB can be well reproduced, as shown in Fig. 2.

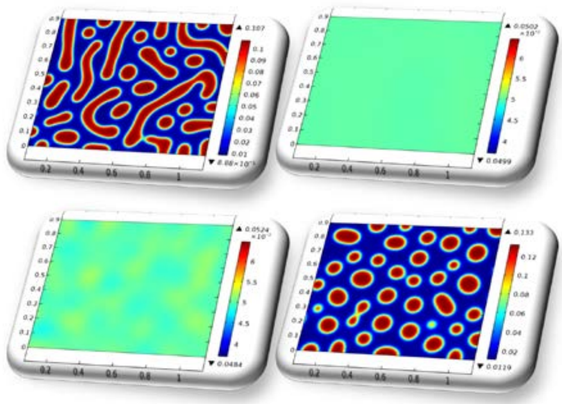

Figure 2. Numerical simulation results of the PMBs after 60 min at 180 °C (upper left for PMB1; upper right for PMB2; lower-left for PMB3; and lower-right for PMB4).

CONCLUSIONS AND PERSPECTIVES

Based on the above described observations and modelling, it can be summarized that the parameters in the phase-field model affect the PMB phase separation behaviour and thus the PMB morphology. They include the mobility, gradient energy coefficients and the parameters related to the local free energy.

The mobility coefficient might depend on the diffusivity of the materials and essentially controlled by mobility of the atoms composing the materials. The gradient energy coefficient is related to the interfacial properties of the PMB. The controlling parameters for the local free energy characterize the interaction between the polymer modifier and bitumen. More research still needs to be done on these parameters and the model towards the development of an applicable tool.

The developed tool will benefit the PMB design by its impacts on the selection of raw materials, the optimization of formula and conditions for PMB production. The tool will also help with increasing the efficiency of facilities and energy use for PMB storage and quality control. Furthermore, with such a tool available, the development of new polymer modifiers for new PMBs can be expected.

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