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Indices for self-healing performance assessments based on molecular dynamics simulation of asphalt binders

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ABSTRACT

Understanding the self-healing mechanism and efficiently evaluating healing potential of asphalt materials is a crucial topic, which is especially necessary for a precise prediction of fatigue life. Most existing laboratory test methods to evaluate healing are empirical or phenomenological in nature, leading to an underestimation of fatigue life significantly. Self-healing processes are inherently of hierarchical, multiscale character. Therefore, researches of healing mechanisms may effectively require discrete atomistic treatments. In this paper, molecular dynamics (MD) simulation was used as a tool to examine the hypothesis of healing mechanism and evaluate the self-healing capability of neat and SBS modified asphalt binders. Densities and glass transition temperatures of neat and SBS modified asphalt binders were figured out based on the MD simulation results. An artificial crack was created in MD model to simulate the diffusion of molecules across a crack interface. Three indices calculated from MD simulation results were put forward to evaluate the self-healing capability of asphalt binders, including diffusion coefficient, activation energy, and pre-exponential factor. Finally, the values of these three indices obtained from MD results were compared with the values derived from fatigue-rest-fatigue test, to assess the reliability of above indices as self-healing performance indicators.

1. Introduction

Extending the fatigue life of asphalt pavement means reducing the usage of asphalt, which would be helpful to posing minimal environmental risk in the case of release of pollutants from asphalt. Fatigue damage is a common type of distress in asphalt pavement. The formation of a fatigue macrocrack always comes from the coalescence of several independently initiated microcracks [31]. However, some microcracks will be healed during the rest period between the loading cycles, leading to the fatigue life extension. This phenomenon is known as self-healing [4,7,30,13,5]. Evidence in the literature indicates that healing plays an important role in improving performance of asphalt mixtures. However, the underlying mechanism of self-healing has not been well understood yet. Most existing laboratory test methods to evaluate healing are empirical or phenomenological in nature, generally applying a continuous fatigue load to the sample until it gets a certain damage, and then allowing it to recover over a period of time [26,34,8,22], and eventually evaluating healing property by comparing the performances (e.g. modulus and stiffness, fatigue life) before and after the rest periods. These healing indices are dependent on the test parameters (e.g., temperature, loading modes, and specimen geometry), which causes some contradictory conclusions on the self-healing capability of asphalt binder, especially when the effect of modifiers is considered [20,6,16]. Therefore, understanding the self-healing mechanism and efficiently evaluating healing potential of asphalt materials become a top issue.

In general, healing process can be hypothesized to be the reverse process of cracking, which contains two important phases namely crack closure and strength gain [25]. Bhasin et al. [2,3] proposed a model, based on the self-healing mechanism in polymers [35,17], that describes self-healing as a combination of wetting and intrinsic healing processes. According to this model, wetting is dependent on the surface free energy of asphalt binder, and subsequent long term self-healing is depend on the self-diffusion of asphalt molecules across the crack interface. From above description, it can be recognized that self-healing processes are inherently of hierarchical, multiscale character. Healing behavior can arise at a myriad of length scales ranging from atomic to microscopic to mesoscopic to macroscopic. Therefore, researches of healing mechanism may effectively require discrete atomistic treatments.

Molecular dynamics (MD) simulation is a computer simulation with atoms and/or molecules interacting using some basic laws of physics [27]. Molecular dynamics simulation provides the

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methodology for detailed microscopic modeling on the molecular scale. Beginning in theoretical physics, the method of MD gained popularity in materials science since the 1970s. Molecular simulation has been gradually applied in the research field of asphalt materials, to understand the behavior of asphalt binders.

Asphaltenes play an important role within the asphalt binder and contribute strongly to the overall mechanical response. Most of molecular simulations related to asphalt binders have largely focused on modeling of asphaltene molecules [24,29,15,10]. Since computational speed increases a lot, large molecular dynamics simulation of asphalt has been studied [23,37,38,39,40,11,36]. Pauli et al. [23] used correlations to estimate properties of the average molecular structures proposed for the core asphalt of SHRP (Strategic Highway Research Program). Zhang and Greenfield [37–39] created a representative asphalt binder containing three different types of molecules: asphaltenes, saturates, and naphthene aromatics, which for the first time used multiple compounds in the same system to simulate the properties of asphalt binders by molecular dynamics (MD) simulation. They studied the dynamics within the asphalt model, and evaluated the influence of polymer modifiers on the properties of asphalt binders [40]. Based on the Zhang and Greenfield's model, Ding et al. studied the influence of SBS modifier on molecular agglomeration behavior of asphalt by analyzing the different radial distribution functions [11]. Bhasin et al. built a system including a microcrack to study the self-healing property of asphalt binders [1]. They calculated the diffusion coefficients of interface, the results showed good correlation with the predefined chemistry parameters and consistency with the experimental findings from FTIR spectroscopy [18].

In the following study, we use molecular dynamics (MD) simulation as a tool to examine the hypothesis of healing mechanism and evaluate the healing capability of neat and SBS modified asphalt binders. Three types of molecules representing different constituent species (asphaltenes, naphthene aromatics, and saturates) in neat asphalt were considered in the MD model. The influence of SBS (Styrene–Butadiene–Styrene) modifier on the self-healing property of asphalt binder was also investigated by adding SBS molecules to the neat asphalt model. Densities and glass transition temperatures of neat and SBS modified asphalt binders were figured out based on the MD simulation results. An artificial crack was created in MD model to simulate the diffusion of molecules across a crack interface. Three indices calculated from MD simulation results were put forward to evaluate the healing capability of asphalt binders, including diffusion coefficient, activation energy, and pre-exponential factor. Finally, the values of these three indices obtained from MD results were compared with the values derived from the fatigue-rest-fatigue test, to assess the reliability of above indices as self-healing performance indicators.

Therefore, the objectives of this study are to (1) use molecular dynamics simulation to examine the hypothesis of healing mechanism, improving the knowledge and understanding the self-healing mechanism of asphalt binders; (2) determine the efficacy of using activation energy and pre-exponential factor as a measure of asphalt self-healing behavior; (3) define the effect of SBS modifier on the self-healing property of asphalt binders.

2. Methodology

2.1. Preparation of molecular structure for simulation

The composition of the asphalt is quite complicated; therefore, it is too difficult to separate each component. Usually, it would be separated into three parts based on its solubility in different solvents. The three parts are as follows: asphaltene, naphthene aromatic, and saturate. The approach of building MD model is to assemble of three different components, which was proposed by Zhang and Greenfield [37,38,39]. Zhang and Greenfield used n-C_{22} and 1,7-dimethylnapthalene to represent saturate and naphthene aromatic, respectively. The adopted asphaltene structure was originally proposed by Groenzin and Mullins [14]. Using these molecules to represent each part, keeping the overall composition close to the total C/H ratio of the real asphalt, and considering the alkane/aromatic carbon ratio reported by Storm et al. [32], a relatively real asphalt model was created. The weight proportion of asphaltenes, saturates, and naphthene aromatics is approximately 20–20–60, respectively.

In this study, we applied above composition method to build neat asphalt models. To investigate the effect of SBS modifiers on the self-healing property of asphalt binders, a linear structure SBS was added to the asphalt model. The structure of SBS (n = 6, m = 3) was referenced from Ding et al. [11]. The established system had 4799 atoms and 5.7% (by weight of asphalt) SBS modifiers. The resulting compositions of neat asphalt model and SBS modified asphalt model are listed in Table 1.

2.2. MD model building and verification

The first step in molecular dynamics simulation was to create the constituent molecules, molecular structures of three parts and linear SBS are illustrated in Fig. 1. The constituent molecules were used to construct an amorphous cell, which is a three-dimensional periodic cubic lattice containing constituent molecules. Periodic boundary conditions were used, indicating that asphalt binder system is surrounded on all sides by replicas of itself, forming an infinite macro-lattice.

In simulation systems, the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field [33] was used, requiring parameters for each atom. The atom-based summation was applied for the van der Waals interactions with a cutoff distance of 9.5 Å (1 Å = 0.1 ns). To optimize the geometry structures and eliminate the unfavorable contacts, the initial configurations were subjected to 10,000 iterations of energy minimization by smart minimizer. Fig. 2 illustrates amorphous cells representing the neat and SBS modified asphalt model, which have the lowest energy.

To ensure that this simulation approach and experimental parameters could provide accurate results, density simulation was first performed on individual asphalt systems. Molecular dynamics simulation was conducted for both systems at 1 atm pressure and nine different temperatures: 150, 200, 225, 250, 275, 298, 323, 348, and 373 K.

Table 1
Compositions of asphalt binders.

Asphalt binder	Number of molecules				Mass fraction (%)
	Asphaltene	Naphthene aromatic	Saturate	SBS	
Neat asphalt	5	30	45	0	20.1–59.8–20.1
SBS modified asphalt	5	30	45	1	19.0–56.4–18.9–5.7