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Modulus simulation of asphalt binder models using Molecular Dynamics (MD) method

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HIGHLIGHTS

- Simulate asphalt binder modified with xGNP using the MD method.
- Analyze different modulus properties of these asphalt binder models.
- Temperature-modulus trends of models were comparable to those of the laboratory data.

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ABSTRACT

The objectives of this study are, 1) to simulate asphalt binder modified with exfoliated multi-layered graphite nanoplatelets (xGNP) using the Molecular Dynamics (MD) method, and 2) to analyze different modulus properties of these asphalt binder models compared with those of the control asphalt binder model. The multi-layered graphene model was used to represent the xGNP particles, which were used to modify the control asphalt in the laboratory. The three-component control asphalt binder model was used as in the authors' previous study. The xGNP modified asphalt binder model was built by incorporating the xGNP model and control asphalt binder model and controlling mass ratios to represent the laboratory prepared samples. After the xGNP modified asphalt binder model was generated, the densities of the control and xGNP modified asphalt binder models were computed and verified. Mechanical properties of these models were simulated and calculated in MD simulations using procedures similar to those in the experiments, which include the bulk modulus, Young's modulus, shear modulus and Poisson's ratio. The simulation results indicate that the temperature-modulus trends of these asphalt binder models were comparable to those of the laboratory data. The MD simulation data were larger than the laboratory results due to limitations of the current MD simulation, which are discussed in this study. In addition, Poisson's ratios calculated from the MD simulations coincided with the laboratory results.

1. Introduction

Nowadays, asphalt pavement is the main type of pavement used around the world, and the performance, properties, and composition of asphalt are studied by researchers. Asphalt is composed of carbon, hydrogen and some trace elements [1–4]. The performance of asphalt also depends on the source and ambient temperatures. Different modifiers have been applied to the original asphalt in order to obtain better pavement performance. Rubber particles [5–10] and fibers of different sizes [11–13] have been widely utilized to enhance the high-temperature performance of asphalt binders and mixtures and, recently, nanomaterials have been used [12,14–16]. The modification mechanism of these modifiers was also explored and the microstructure of the modified asphalt was examined by researchers [5,14,17–21]. However, the fundamental understanding of the modification and interaction between the modifiers and asphalt are still unclear on a nanoscale in the modified asphalt materials.

Molecular dynamics (MD), originating from physics, is widely applied in different research areas. It is a computer program used to simulate the materials and their behaviors on the atomic scale [22]. The physical movements and interactions of atoms and molecules are simulated for a specific period of time. The trajectories of

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atoms and molecules are recorded based on the solution of Newton's equation of motion for the interacting particles, where forces and energies between the particles are calculated by the force field [23]. At present, the molecular dynamics (MD) method is a new tool for researchers to understand the physical properties of materials and functions of macromolecules on the atomic scale. MD describes the details of each particle/atom motion over a period of time, and it helps address some specific problems or principles of atoms or materials. It is easier than doing the experiments in the laboratory. In MD simulation, a specific property of materials can be solely studied by altering the specific contributions, and it can be used for fundamental research or functional predictions of a new material. There are many differences between the MD simulations and other numerical tools: 1) inputs in the MD model are descriptions of interatomic and intermolecular interactions, which are different from other numerical tools. Most inputs from other tools are modulus, stiffness, or other parameters; 2) no assumptions are required for processes or mechanisms, whereas other tools may need assumptions for mechanisms; 3) detailed molecular or atomic level information is provided while other tools cannot provide atomic information; 4) the results are more reliable compared to other numerical tools.

The asphalt material was simulated with three different components [3] and four different components [24,25]. With three kinds of components, two different asphaltenes, saturates and naphthene aromatics were first used to build the three-component molecular model of asphalt [3]. Different properties of the asphalt binder models, such as density, thermal expansion, isothermal compressibility, and bulk modulus, were calculated and evaluated with the All-atom Optimized Parameters for Liquid Simulation (OPLS-aa) force field [3]. When using four kinds of components, an asphalt binder model, which is similar to the asphalt AAA-1 of the Strategic Highway Research Program (SHRP) [24], was generated with seven components. The composition of this model consists of asphaltene, polar aromatic, naphthene aromatic, and saturate [24]. The Hansen solubility parameters of components in the asphalt binder models were calculated, and the radial distribution function and intramolecular orientation of components were also analyzed [24]. The new compositions of asphalt models were proposed to represent the AAA-1, AAK-1, and AAM-1 asphalt with twelve molecules, and the partial charges and force field parameters were determined through quantum mechanics. The Hansen solubility parameters were used to understand the components in asphalt models. The densities of the new models are better than those of prior models [25]. Based on these references, the feasibility and validity of the MD application in asphalt materials were demonstrated, however, the predicted accuracy and algorithms or methods used for analysis need to be improved.

The objectives of this study are as follows: apply the Molecular Dynamics (MD) method to simulate and calculate the moduli of the control and xGNP modified asphalt binder models and compare these values with the laboratory results. The modulus properties include the bulk modulus, Young's modulus and shear modulus. In this study, the control asphalt binder model was composed of asphaltenes, naphthene aromatics, and saturates, based on the Corbett method [2]. The graphite model with the multi-layer molecular structure was used to represent exfoliated multi-layered graphite nanoplatelet (xGNP) particles as a modifier for this study. The modified asphalt binder model was built by incorporating the xGNP model and control asphalt binder model and controlling the mass ratios to represent the laboratory prepared samples.

Mechanical modulus properties of the asphalt binder models were analyzed with different MD simulation methods: 1) compute the bulk modulus of the asphalt binder models through compressive and expansive volumetric strain-pressure relations; 2) simulate the Young's modulus of these models by applying the compressive and tensile strain in one direction at different temperatures, and then, calculate stress/strain ratio in that direction; 3) calculate the shear modulus of the models by applying a shear strain in the XY direction at different temperatures, and then, compute shear stress/strain ratios; and 4) analyze Poisson's ratio of the models using the relationship between Poisson's ratio and the moduli (bulk modulus and shear modulus).

2. Force field

The force field, a kind of energy function, provides the parameters for every type of atom in the MD simulation to calculate the energy of the system. The parameters of the energy functions can be derived from the physical and chemical experiments, as well as from the calculation results of quantum mechanics. The basic functional form of energy in MD simulations includes bonded and nonbonded terms. The bonded terms for interactions are described by covalent bonds, and nonbonded terms are represented by long-range electrostatic and van der Waals forces. The Amber Cornell Extension Force Field (ACEFF) was used based on the Amber Cornell Force filed [26] in this study, and some experimental parameters were obtained from the General Amber Force Field (GAFF) [27]. The formula for energy calculation of ACEFF is shown in Eq. (1). The NWChem [28] was used to optimize the geometry and calculate the electrostatic potential (ESP) charge for each component of the asphalt binder model. When assigning the ESP charge to atoms, the density functional theory (DFT) module was adopted for optimization and charge fit.

$$E_{total} = \sum_{bonds} K_r(r - r_{eq})^2 + \sum_{angles} K_\theta(\theta - \theta_{eq})^2 + \sum_{dihedrals} \frac{V_n}{2}[1 + \cos(n\varphi - \gamma)] + \sum_{i<j} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}} + \frac{q_i q_j}{\epsilon R_{ij}}\right] \quad (1)$$

where r_{eq} or θ_{eq} is the equilibrium of the structural data; K_r is the force coefficient between double bonds; K_θ is the force coefficient from vibrational analysis; n is the multiplicity for dihedrals; γ is the phase angle for the torsional angle parameters; A, B and q are the non-bonded potentials; q_i and q_j are charges of two atoms, and the charges were calculated and obtained from NWChem analysis; R_{ij} is the distance between atoms; and ϵ is the depth of the van der Waals energy well.

3. Energy optimization and asphalt binder models

3.1. Model optimization methods

The xGNP modified asphalt binder model (Fig. 1b) was optimized by the conjugate gradient method (a kind of algorithm to solve optimization problems) and the Particle-Particle-Particle-Mesh Method (PPPM) (an accurate and efficient method to calculate interactions in MD simulation) [29]. The conjugate gradient method was used to relocate the positions of atoms and reallocate the velocities of atoms in asphalt binder models [30,31]. Based on the equation and calculation of force fields, the positions of atom relates to the energy calculation and the velocities of atoms relate to the moment of the atoms. The conjugate gradient method was used to optimize the positions and velocities for energy and parameter optimizations. The conjugate gradient method is often used as an iterative method (Eq. (2)) for large systems to resolve unconstrained optimization problems, such as energy optimizations in MD simulations, which cannot be optimized by direct methods. The PPPM (a kind of Ewald summation) was used to optimize the system energy by mapping charges to a three-dimensional mesh and using three-dimensional fast Fourier