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Molecular dynamics study of oxidative aging effect on asphalt binder properties

Guangji Xu, Hao Wang *

Rutgers, The State University of New Jersey, Piscataway, NJ 08854, United States

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ABSTRACT

The oxidative aging effect of asphalt binder was investigated using molecular dynamics simulation in this study. Representative molecular models of aged asphalt were built by introducing ketone and sulfoxide function groups into virgin asphalt. The asphalt molecular models were validated in terms of thermodynamic properties such as density, surface energy, viscosity, and cohesive energy density. The molecular structures of virgin and aged asphalt were analyzed by mean square displacement (MSD) and radial distribution function (RDF) of molecules and diffusion coefficient. The aging effect on self-healing potential and moisture damage susceptibility of asphalt were investigated. Results show that the molecular structure of asphalt is in agreement with the colloidal theory. Aging weakens the nano-aggregation behavior of asphaltene molecules and reduces the translational mobility of asphalt molecules. Compared to virgin asphalt, aged asphalt has the higher activation energy barrier for self-healing. Inclusion of water molecules in the asphalt-aggregate interface causes degradation of work of adhesion and this effect is more significant for aged asphalt. The research findings provide insights to better understand the chemo-physical and chemo-mechanical relationships of asphalt-based materials.

1. Introduction

As one of the common adhesive materials, asphalt has been widely used in transportation, building construction, and industrial applications. Up to the present asphalt has been used in more than 90 percent of paved roads in the United States [1]. The aging process occurs in asphalt pavements in two stages. Short-term aging occurs when asphalt is subjected to heat and air in the process of asphalt mixture production and paving, which is primarily due to oxidation and loss of volatile component at high temperatures. Long-term aging of asphalt occurs over the service life of road pavement, which is mainly progressive oxidation. Therefore, understanding asphalt aging effect is important for asphalt material design to achieve longevity and durability.

The detailed mechanism for asphalt aging is still uncertain due to the complexity of chemical compositions of asphalt. One most common aging mechanism is oxidative aging, where oxygen reacts with reactive components of asphalt and changes its physical and mechanical properties [2]. The formation of oxidation products changes chemical compositions of asphalt and leads to an increase of the overall stiffness and brittleness [3]. Although the hardening of asphalt could be beneficial by enhancing rutting resistance of pavement, aging could be detrimental for accelerating pavement distresses and causing premature failure.

Asphalt chemistry links closely to thermodynamic properties and performance characteristics of asphalt. Aged asphalt, with the introduction of oxygen atoms and the formation of oxidation products, differs from virgin asphalt in terms of chemical structure [4,5]. From a fundamental point of view, asphalt compositions at the molecular level, together with the interaction among different molecular groups, determine the overall performance of asphalt material.

Recently, developments of material characterization technology help better understand asphalt aging effect at the micro and macroscopic levels. A number of experimental studies have been carried out evaluate the aging effect of asphalt binder on rheology, mechanical properties, and durability (such as cracking and stripping potential) [6–8]. However, asphalt aging, by nature, is a phenomenon caused by asphalt chemistry changes at atomic to molecular scales. Molecular dynamics (MD) simulation has been proved to be a powerful computational method for material design since it has the inherent advantage to predict manifold aspects of material properties at the molecular levels. This makes it meaningful to investigate asphalt aging effect using MD simulations.

* Corresponding author.
E-mail address: hwang.cee@rutgers.edu (H. Wang).

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Asphalt is a dispersion of polar molecules in a solvating medium composed of less polar asphalt molecules. The oxidation products greatly alter the state of dispersion of asphalt components and molecular mobility [4]. The chemical nature of aging is related to molecular movement and reconstruction. Although it is generally difficult to simulate molecular composition changes and chemical reactions during the aging process using the classical MD, it is possible to evaluate the aging effect using different molecular models of virgin and aged asphalt based on aging mechanism and experimental observations. Such evaluation can help better understand the effect of chemical changes due to aging on rheology and performance of asphalt.

2. Objective

The objective of this study is to investigate oxidative aging effect of asphalt on thermodynamic and performance-related properties using molecular dynamics simulation. Molecular models of virgin and aged asphalt binder were constructed with saturates, aromatics, resins and asphaltenes (SARA) fractions. The validation of molecular models was conducted by means of a variety of thermodynamic properties including density, surface energy, viscosity, and cohesive energy density. Asphalt molecular structures of virgin and aged asphalt were compared using radial distribution function (RDF) and mean square displacement (MSD) that indicates the arrangement and interactions of SARA fractions and translation mobility of asphalt molecules. The performance-related properties of asphalt, such as self-healing potential and moisture damage susceptibility, were investigated through MD simulations of the cracked surface model and the asphalt-aggregate interface model, respectively.

3. Simulation models and methods

3.1. Virgin and aged asphalt models

It is difficult to obtain the detailed information on chemical components of asphalt, which is a complex chemical mixture. Thus, asphalt was divided into different fractions by modern separation techniques, according to their similar polar and molecular characteristics. At the molecular level, asphalt is a mixture of a wide variety of hydrocarbons, together with heteroatoms such as nitrogen, sulfur, oxygen, and metals.

The 12-component asphalt model, first proposed to represent SHRP core asphalt AAA-1, was used to represent the virgin asphalt binder following the suggestions in the literature [9]. Slight modifications, such as side group locations, were made to optimize molecular configuration. Fig. 1 shows molecular models of virgin and aged asphalt following SARA classification system (S for saturates, first A for asphaltenes, R for resins and the second A for aromatics). The details of asphalt molecular system composition and the number of atoms are listed in Table 1.

Three different molecular structures are used to represent asphaltene fraction, which is the most polar component with biggest size in the asphalt system, as shown in Fig. 1(a). These asphaltene structures are originally proposed by Mullins, and they are asphaltene-phenol, asphaltene-pyrrole and asphaltene-thiophene, respectively [10]. Resins, also called polar aromatics, are composed of polar aromatic rings and non-polar paraffinic groups. Heteroatoms such as oxygen, sulfur and nitrogen are found in rein molecules and it is the second polar fraction in asphalt. Resin acts as a stabilizer for the asphaltene and thus plays an important role in asphalt stability [11].

Fig. 1(b) illustrates the five molecules used to represent resin fraction, and namely they are quinolinohopane, thioisorenieratane, benzobisbenzothiophene, pyridinohopane and trimethylbenzene-oxane [9]. The aromatics, sometimes referred as naphthene aromatics, are hydrocarbons structures with light molecular weights as well as minimal polarity in asphalt system. Two molecular models, perhydrophenanthrene-naphthalene (PHPN) and dioctyl-cyclohexane-naphthalene (DOCHN), were selected as representative aromatic fraction, as shown in Fig. 1(c) [9]. Resins, together with aromatics, are the most abundant fractions within asphalt. Saturates contain aliphatic chain structures with branching and cyclic alkanes. Saturates are the least sensitive to oxidative aging and rarely change with time due to lack of polar atoms or aromatic rings. Squalane and hopane, which are shown in Fig. 1(d), are adopted as saturates molecules [9].

Previous research has found that asphalt materials exhibit similar kinetics during the oxidative aging, and in general there are two periods are included. The first is an initial fast reaction period, which is followed by a slower reaction period with a nearly constant rate. In the two reaction periods, the hydrocarbon chemical reactions are known to be fundamentally different. In the process of the rapid oxidation spurt, sulfoxides are the major oxidation; while for the slower reaction period, ketones are the major product. The ratio of ketones to sulfoxides formed was found dependent on oxygen concentration (pressure), temperature, and sulfur content [12].

Extensive experimental studies have been carried out to study the mechanism of asphalt aging due to oxidation. It was found that certain types of carbon and sulfur compounds in asphalt are susceptible to oxidation. The ketones and sulfoxides have been identified as major functional groups formed after oxidation [4,13]. For example, benzyl carbon, the first carbon bonded to an aromatic ring, is a readily oxidizable site [14]. Ketone is formed when oxygen replaces the hydrogen atom attached to the benzylic carbon atom. Therefore, as illustrated in Fig. 1, the function groups of ketone and sulfoxide were added to the possible oxidizable locations of virgin asphalt molecular models [15], representing aging effect in asphalt binder. It is noted that the saturate fraction models were assumed the same before and after oxidation aging. The mass fraction of each molecular component was chosen to model asphalt molecular system closest to the real asphalt. In addition to ketones and sulfoxides, other polar groups (such as carboxylic acids and phenols), may be also important carbonyl group products generated during asphalt aging, which should be considered in future studies.

3.2. Force field and simulation detail

Molecular Dynamics (MD) simulations were performed using commercially available simulation software, Materials Studio [16]. To describe molecular interactions and intermolecular potential, COMPASSII (Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field was used. COMPASSII has a wide and detailed coverage in materials such as most common organics, small inorganic molecules, and polymers, and it also has been validated to enable accurate prediction of related material properties [17]. COMPASSII is a significant extension to the COMPASS force field in terms of atom types and force field terms.

In the following all-atom molecular dynamics simulation, atom based summation was applied for van der Waals interactions with a cutoff distance of 15.5 Å, and long range correction was applied beyond that distance. As for the electrostatic interaction, Ewald summation method with a 6 Å cutoff distance was used. Nose-Hoover thermostat and barostat were applied to control the temperature and pressure of systems. All the simulations were performed with a time step of 1 fs.

To build the virgin and aged asphalt model, the assigned numbers of each type of molecule were first put into a big cubic box