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Full Length Article

Molecular dynamics modeling and simulation of bituminous binder chemical aging due to variation of oxidation level and saturate-aromatic-resin-asphaltene fraction

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ABSTRACT

Bituminous binder's chemical aging process leads to significant changes in its mechanical and rheological properties. The two main outcomes of chemical aging are the oxidation of molecules and changes in the binder's saturate-aromatic-resin-asphaltene (SARA) fractions. The binder components' reaction to oxygen results in the formation of polar viscosity-building molecules, while changes in the SARA fractions disturbs the binder's balance, giving it brittle properties. As both of these factors affect the binder at the molecular level, molecular dynamics (MD) simulations can improve the fundamental understanding of binder aging. Therefore, nine MD models were built (one model that represents unaged binder and eight different aged binder models) in this study for two specific purposes: to compare the MD simulation results with the experimental results and to conduct a parametric analysis of the MD simulations to investigate the effect of each aging outcome on the properties of the binder. A comparison among binders with different aging levels showed that the MD simulations and experiments had the same rank order in viscosity values, but they had significantly different magnitudes, which may be partly attributed to the high shear rates used in the MD simulation. The parametric analysis indicated that the dominant aging mechanism in the laboratory aged binder was the disturbance of the SARA fractions, while the oxidation of the molecules appears to be a more dominant mechanism in the field aged binder.

1. Introduction

Bituminous (asphaltic) binder is a multi-component material with almost one million types of molecules, which range from small to large and polar to nonpolar [1]. The mechanical, physical and chemical properties of asphalt are governed by the configuration and interaction among the molecules [2,30]. This complexity makes it extremely difficult to characterize the chemical structure of binder's elements and predict its properties.

During pavement construction and throughout its long-term service life, bituminous binder interacts with different environmental factors and undergoes chemical changes that alter its properties. This process is known as chemical aging, and it typically leads to reduced binder ductility and increased brittleness, making the binder more susceptible to distresses, such as cracking [3,40]. Various factors affect pavement during its service life, which makes it difficult to fully understand the mechanisms behind aging. Several methods have been used to characterize aging, ranging from the analyses of different binder fractions to the elemental analysis and Fourier transform infrared spectroscopy of the asphaltic binder.

When asphalt is exposed to atmospheric oxygen, it oxidizes and forms polar functional groups that alter the rheological properties of the binder [4,39]. Ketone and sulfoxide functional groups are major products of binder's oxidative aging [5]. Ketones are formed when the hydrogen atom attached to the benzylic carbon atoms is replaced by oxygen. Benzylic carbon is the carbon atom adjacent to an aromatic ring system, and it is binder's most sensitive hydrocarbon [6]. Sulfoxides are a chemical functional group that contain sulfinyl (S=O)

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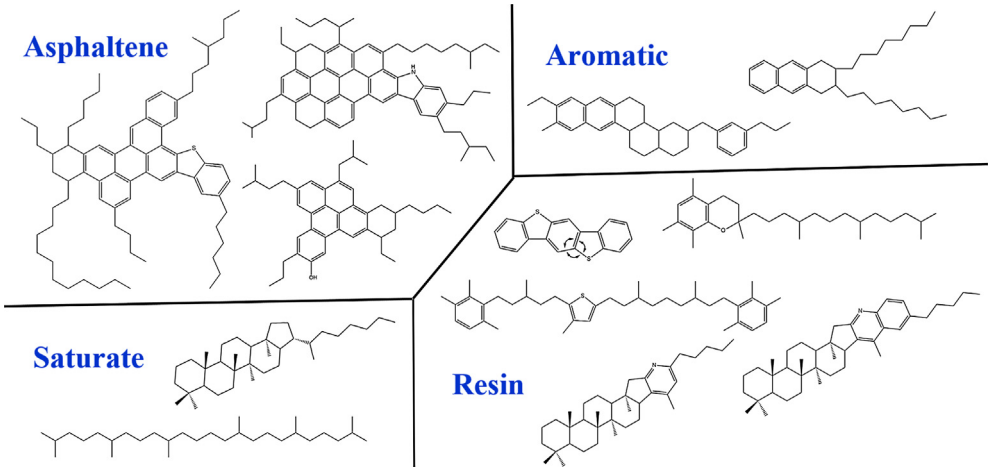

Fig. 1. The binder molecules used to form the MD models and conduct the simulations.

attached to two carbon atoms. The sulfoxides formed with sulfur atoms are major products of oxidative aging.

Asphalt binder is typically characterized by its hydrocarbon class composition, namely saturate-aromatic-resin-asphaltene (SARA) composition [30]. These fractions can be separated based on their size and solubility in polar, non-polar, or aromatic solvents using the selective adsorption–desorption method proposed by Corbett [7]. An increase in the resin and asphaltene fractions and a decrease in the aromatic content of the asphalt occur during the aging process, when the aromatic fraction is believed to convert to resin and the resin is then believed to convert to asphaltene [8].

Given that the exact chemical composition of asphalt binder cannot be determined, studies have used representative molecules in molecular dynamics (MD) simulations to model binder behavior. Li and Greenfield [9] proposed a 12-component model of asphalt binder to represent the AAA-1, AAK-1, and AAM-1 of the Strategic Highway Research Program (SHRP). The molecular structures were proposed based primarily on geochemistry literature's analysis of the petroleum found in sedimentary rock deposits. The characteristics of the models agreed well with the elemental and SARA analysis results specific to each binder. They achieved densities that were closer to the experimental values than previous asphalt models. Martín-Martínez et al. [10] proposed modifications to the asphaltene molecules used by Zhang and Greenfield [11] and Li and Greenfield [9], which led to lower internal energies and a higher probability of occurrence in asphalt. Based on the Clar sextet and density functional theories, the distribution of p electrons in the polycyclic aromatic core may be optimized and the geometrical strain within the molecule may be minimized.

MD simulations have been used to provide insight into the molecular interactions and aging mechanisms of bituminous materials [31–34]. For example, Bhasin et al. [12] investigated the self-healing phenomenon in asphalt binders and demonstrated a correlation between the chain length and self-diffusivity of the molecules at crack interfaces, which influences the rate of intrinsic healing in asphalt binders. Lemarchand et al. [32] used the four-component united-atom "Cooee" bitumen model [31] to calculate shear viscosity of binder at four temperatures. Khabaz and Khare [13] investigated the glass transition and molecular mobility for neat and styrene–butadiene rubber (SBR) modified asphalt. The volume-temperature behavior of the systems exhibited a glass transition phenomenon, but the glass transition temperature of the neat- and SBR-modified binders was not different. Xu et al. [14] investigated the adhesive bonding between binder and silicate minerals in aggregate using different SARA fractions for virgin and aged binders. Pan and Tarefder [15] and Xu and Wang [16] studied the effects of oxidative aging on binder properties by considering ketone and sulfoxide functional groups. More recently, Khabaz and Khare [29] successfully applied time–temperature superposition principle to MD simulation results and constructed master curves of viscosity, dynamic modulus, and tensile creep compliance of asphalt.

2. Study objectives

The two major indicators of chemical aging are the disturbance of the balance among the SARA fractions and the oxidation of the asphalt binder molecules. Both of these processes affect binder at the molecular level, and both occur during the binder's laboratory- and field-aging processes. However, laboratory scale testing is not capable of differentiating between each factor and can only capture their combined effects on the binder properties. This study investigated the effect of each aging indicator on the binder properties. Given that aging mechanisms affect the asphalt binder at a molecular level, investigating such changes in the binder's macroscale properties using MD simulations may provide insights into the chemical aging process. Therefore, different binder MD models were built with the following two specific objectives:

- To compare the MD simulation results with the available experimental results and assess whether the MD results can realistically capture the effects of aging;
- To conduct a parametric analysis of the MD simulations by varying each aging indicator (i.e., oxidation and SATA fraction) to investigate how changes in the binder's molecular level due to aging affect its macroscale properties.

3. Molecular dynamics modeling method

In this study, the asphalt molecules proposed by Li and Greenfield [9] and the asphaltene molecules presented by Martín-Martínez et al. [10] were used to build an asphalt model without additional oxidation. The polar aromatic, naphthene aromatic, and saturate molecules were based on the study by Li and Greenfield [9], and the asphaltene molecules were based on the study by Martín-Martínez et al. [10]. The number of molecules for the models were determined based on laboratory tests, as discussed in the following sections, making the models different from those proposed by Li and Greenfield [9]. Fig. 1 shows the unoxidized molecules for each fraction.

Oxidized molecules were then developed by adding oxygen atoms to the sensitive chemical functional groups of the unoxidized binder molecules. Two major products of oxidative aging include the ketones formed at the benzylic carbon atoms and the sulfoxides formed in the sulfide functional groups [5]. Therefore, based on the oxygen content necessary for each binder MD model, different numbers of oxygen